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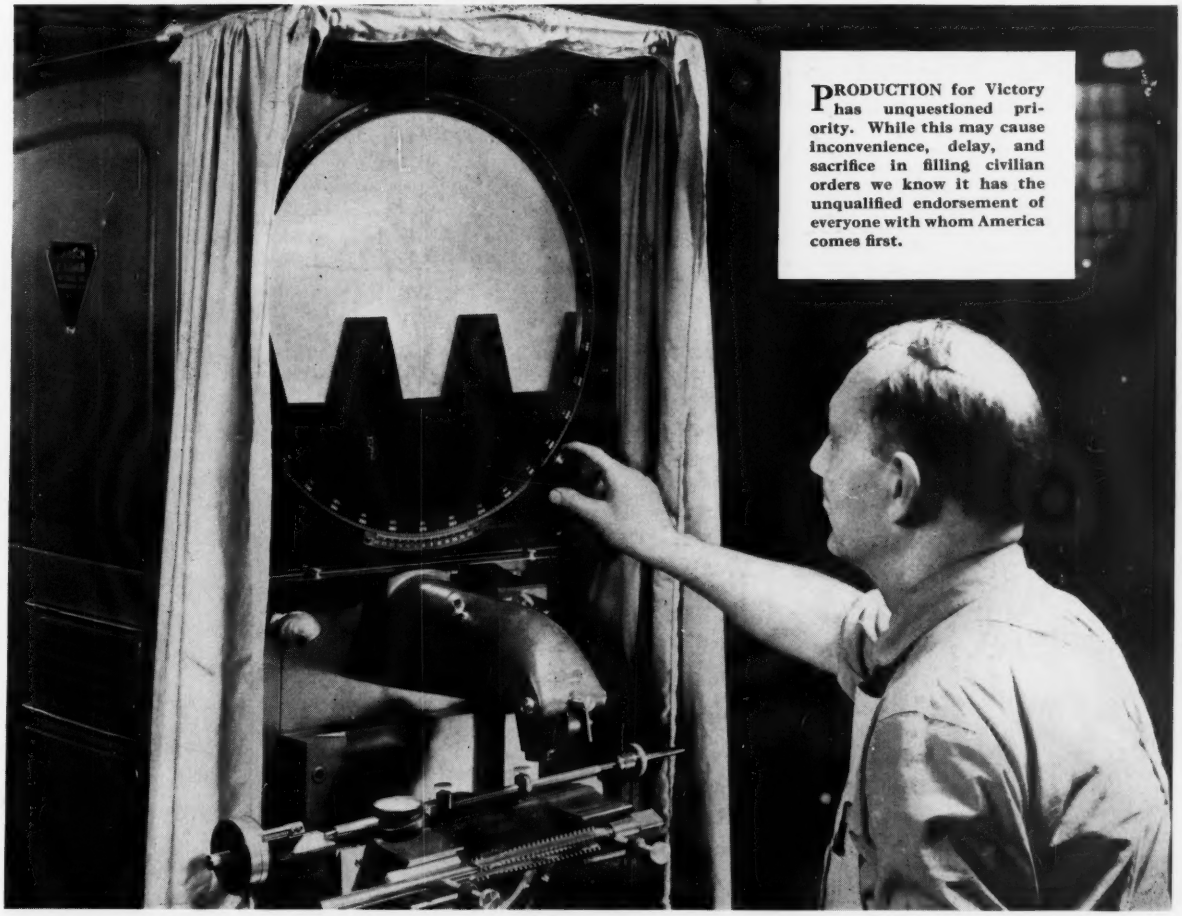
CHEMICAL EDUCATION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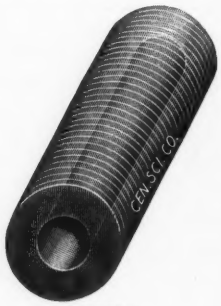

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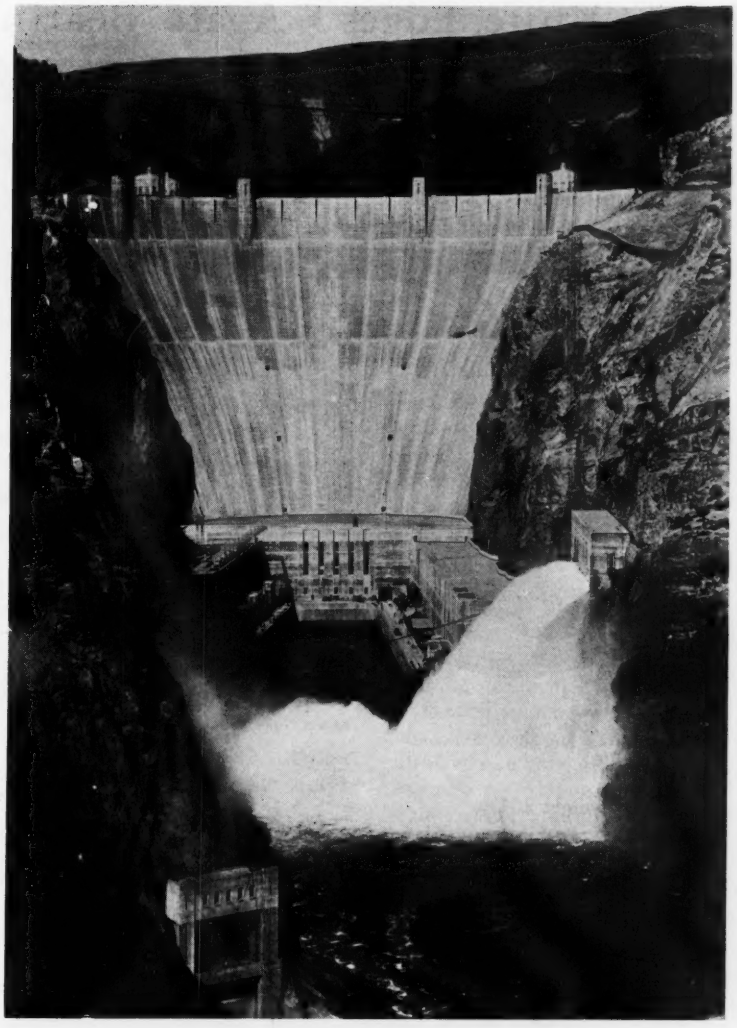

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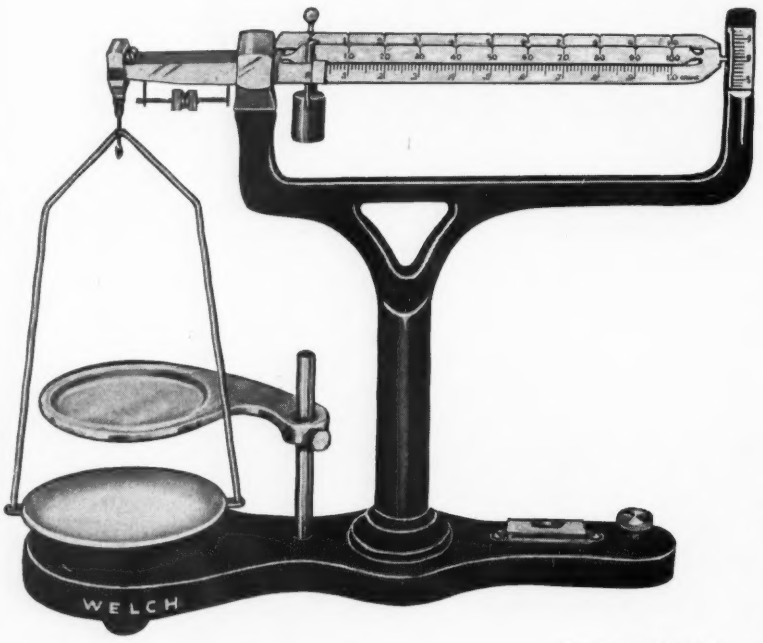

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Editor's Outlook

WE HAVE long had it in mind to write a short homily on professional spirit among chemistry teachers. This is it. Anyone who feels he doesn't need it, or that the subject bores him, need read no further. It probably wouldn't do him any good. While this is particularly directed to secondary-school teachers it is not without its point for many college instructors as well.

What brought this intention to accomplishment was the last editorial reading of the article on "Origin and Transformation of Carbohydrates in Plants," by H. A. Spoehr, in this issue. Here, it strikes us, is a good test of professional spirit. We would like to know the number of teachers who read this article, for we feel it would indicate the proportion whose interest in the profession of chemistry is broader than their own individual specialties and daily routines.

This is an article which is well written, not too difficult for the comprehension of any reasonably well-trained chemist, and still not so elementary as to be trivial. It pays dividends for the intellectual effort expended on it. But we dare say that many teachers will turn the pages, being uninterested in carbohydrates, and failing to realize that they compose a large portion of the substratum of life and that there might be expected of anyone who calls himself a chemist as complete a knowledge as possible of their origin and position in the scheme of things.

Much has been made of the contention that on graduation from college a young man is just in a position to *begin* to learn. But if so, he all too frequently fails to get started. Oh, he quickly enough learns the tricks of a routine, the narrow specialties which bring him an increase in pay. But his experience in the field of chemistry in general often becomes less rather than more. Anyone who has been concerned with programs of professional meetings knows that you can get the rubber chemists out to hear a lecture on rubber and the textile chemists out to hear a lecture on rayon, but the sheep won't eat the food laid out for the goats, and vice versa. Nor will either of these industrial groups, nor any other, stir from their firesides to listen to a lecture on general chemical theory—even if it promises to turn the fundamentals of the science upside down. It simply doesn't concern them. Chemical isolationism!

Now you might not expect this sort of thing to be true of teachers, but it is all too common. Perhaps we are just taking a sock at a tender spot in human nature; nevertheless, we think it deserves to be *socked*. And teachers, too, will have to take it standing up.

Why should teachers expect more from their students than from themselves in the way of general interest and breadth of background? They often do. Too many teachers are completely limited in their interests to the mere routine of their teaching. This lack of professional spirit is indicated by the very small number of high-school teachers in the membership of the American Chemical Society, and also by the fact that their reading is, in general, anything but "professional." They will read, to be sure, what can be directly interpreted in terms of their daily teaching problems. But general self-improvement should be as conscious an aim for teachers as it is urged to be for students. If teachers set so limited a standard for themselves in their intellectual interests they should not object if their students do *their* studying for the sole purpose of passing examinations.

We have great sympathy, nevertheless, for the high-school teachers of chemistry. They serve two masters. Their duty is primarily to the *teaching* profession, not to the chemical profession. Their job is, first, to teach *boys* and *girls*, and second, to teach them *chemistry*. They may be subject-matter specialists (*i. e.*, "professional" chemists) or not, depending upon the particular school, the course of training through which they have come, or the educational philosophy of their superior educational authorities. But nevertheless, they *represent* the profession of chemistry to the pupils in their charge, and if some of them take their subject-matter responsibilities seriously the others will suffer by comparison, in the eyes of the chemical profession at large.

What teacher can do a good job of teaching *boys* and *girls*, even, to say nothing of teaching them anything in *particular*, who has not absorbed the professional spirit of his subject matter enough to be more than a mere repeater-of-the-sayings-of-others?

Last month the gist of our argument was: Students should come to college to get something out of professors. Secondary-school students are even more dependent upon their teachers. Don't let them down; be sure there is something for them to get. We think a student has a right to get his ideas about chemistry from a person whose interest and training are broad enough to warrant his being called a *chemist*.

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A Transparent Phase Rule Model

LIU-SHENG TS'AI

Yenching University, Peking, China

STUDENTS in physical chemistry often find it difficult to visualize the phase rule relation from the diagrams given in the textbooks which are intended to represent a space relationship in three dimensions. To overcome this difficulty various solid models,[1] usually made of plaster, are constructed.

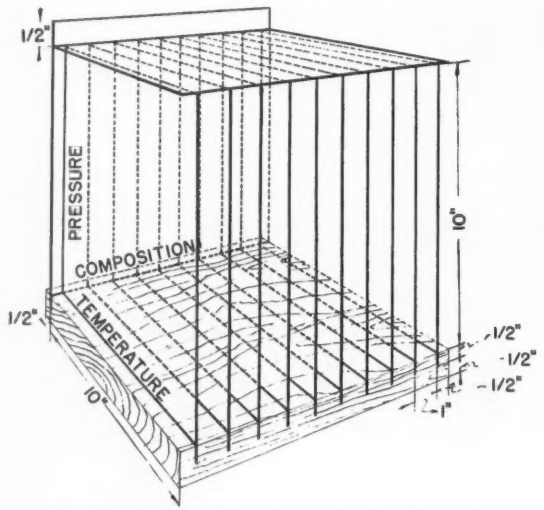


FIGURE 1.—THE TRANSPARENT PHASE RULE MODEL

The disadvantages of this type of model, however, are twofold. First, the construction of such a model is time-consuming, and second, the regions under the surface of the model are not visible. The present article describes a type of model which is easy to construct and, since it consists entirely of glass plates, is transparent. Thick cellophane or pliofilm sheets now available are superior, but more expensive than the glass plates.

Grooves as shown in Figure 1 are cut on a wooden baseboard approximately 10″ × 10½″ × 1″. These grooves are of such dimensions that the glass plates can be held firmly in place and yet may easily be removed if desired. The board may then be painted white. Eleven glass plates, each 10″ × 10½″, and another, 10″ × 11″, are prepared. The arrangement of these plates is shown in Figure 1, the larger plate being placed in the back. The model may now be used to represent either a one-, two-, or three-component system.

For constructing a three-component system, one may use, as an example, the figures given by Taylor.[2] The curves (tie-lines not included) are sketched on each plate as an isotherm. The plates are then arranged in the order of increasing temperatures. The three-dimensional character of the system will then be clearly seen. Similarly, for a one-component system one may use the curves given by Verwiebe[1] (thermodynamic surfaces of CO_2 or H_2O). For a two-component system, the well-known KCl–H_2O system might be used. Curves on the temperature–pressure plane are drawn on each plate for each composition. Inasmuch as the model is primarily for demonstration purposes it is only necessary to sketch the curves roughly. Chinese ink[3] and a Chinese brush can be used for this purpose. Figure 2 shows schematically the curves for the system KCl and H_2O. The solid space can be brought out more clearly both by increasing the number of plates and by coloring different regions with different colored inks.[3] In the region where more than one solid appears (such as in a eutectic mixture) the area may be dotted with different colors to represent different solids. The plate on top of the model may be used for drawing the curves representing any one composition–temperature plane. A single model such as here described may be used to represent different systems since the curves can be easily erased with a damp cloth and new curves drawn.

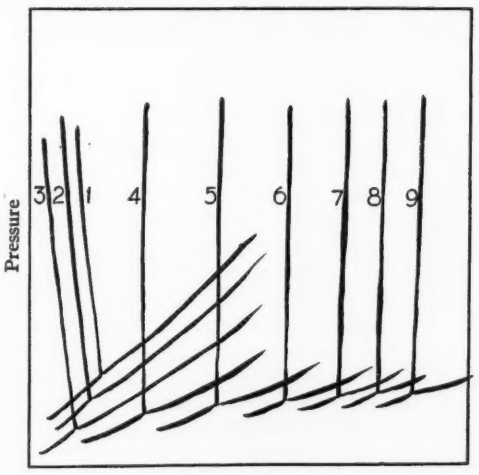


FIGURE 2.—SKETCH OF KCl-H_2O SYSTEM

Each of the numbered curves is drawn on a separate plate and represents the P–T curve for each composition. The order is that of increasing KCl concentration. Curve 3 represents the eutectic composition

[1] VERWIEBE, *Am. Phys. Teacher*, **3**, 180 (1935).

[2] TAYLOR, Editor, "A treatise on physical chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York City, **1931**, p. 576.

[3] Chinese ink can be easily prepared by grinding lampblack in a mortar with enough two per cent gelatin solution to give the proper consistency. Inks of different colors can be prepared in a similar way using colored pigments.

Johann Rudolf Glauber (1604-70)

His Chemical and Human Philosophy[1]

EVA V. ARMSTRONG[2] and CLAUDE K. DEISCHER[3]

University of Pennsylvania, Philadelphia, Pennsylvania

"The world goeth on crutches . . . . Of the mischievous composition and diabolical use of gunpowder much could be written. . . . The present world taketh onely delight in shedding innocent blood, and cannot endure that unrighteous things should be reproved . . . . The honour of God and his command are in no repute, and are trampled under foot . . . . None will leave his contumacy or stubbornness, or recede a little from his opinion although the whole world should be turned upside down thereby. . . . . It is no marvel that God sent such a terrible scourge as gunpowder is upon us; and it is credible, that if this do not cause our amendment, that a worse will follow . . . thunder and lightning falling down from Heaven, whereby the world shall be turned upside down to make an end of all pride, self-love, ambition, deceit and vanity . . . . Woolves are now clothed in sheeps skins, so that none of them almost are to be found, and yet the deeds and works of Woolves are everywhere extant . . . ." (*2*).

THIS is not a picture of the advanced civilization which we enjoy today, but a description of the world in which Johann Rudolf Glauber, German chemist, lived and worked three hundred years ago. At that time Germany was ravaged by the Thirty Years War, carried on not by disciplined armies but by wandering bands of adventurers on plunder bent. Incredible cruelties were inflicted on their victims. Towns and villages were laid waste. Schools and churches were closed. Famine and pestilence stalked the land. So wretched was the condition of the people that cannibalism was not unknown. Literature, art, and science vanished from the scene.

As we go back through the centuries, time stands still. The walls of the years are lined with shelves on which repose in dusty neglect the wisdom of the ages; on the floors lie jumbled heaps of forgotten lore, folly, and superstition, rubbish fouling treasure-trove. As it was in the beginning, so it is today. Nature, secret, changeless, and eternal, challenges the artifice of man; and man, being what he is, accepts the challenge, struggles, prevails a little, and dies.

Johann Rudolf Glauber was one who accepted the challenge. Craving peace and a quiet life in which to study the mysteries of nature, it was his fate to live amid turmoil and strife, and to be driven from one city to another by the exigencies of the times.

He was born at Karlstadt am Main in 1604, the son of Rudolf Glauber, a barber, who combined the duties of hairdresser, dentist, and surgeon in accordance with the custom of the period. While the "barber of the long robe" possessed a modicum of educational training, the "barber of the short robe" was forced to study nature in the raw. In Germany, the barber often served as a keeper of the bath, and his duties included bleeding,

TRUE PORTRAIT OF THE HONORED AND HIGHLY ESTEEMED "HERREN JOHANNIS RUDOLPHI GLAUBERI," NOBLE CHEMIST AND EXPERIMENTER AT KITZINGEN IN FRANCONIA

1654 A. S.

"Just as the heaven's light beautifully brightens the earth,
And all around is dark,
Just like the gaily colored flower beautifies the field,
So art crowns men with honors.
Because 'Herr Glauber' has been given 'Chymie's' gift
From God, he should receive deserved praise from all."[4]

cupping, leeching, the giving of enemas, extraction of teeth, and the preparation and dispensing of salves and plasters. Then, as now, the barber shop was a news cen-

[1] Presented before the Division of the History of Chemistry at the 102nd meeting of the A. C. S., Atlantic City, New Jersey, September 9, 1941.

[2] Curator, Edgar Fahs Smith Memorial Collection, University of Pennsylvania.

[3] Assistant Professor of Chemistry, University of Pennsylvania.

[4] The original etching of Glauber, after having been lost for 250 years, came to light in the famous collection of W. Drugulin, who ascribed the portrait to Anthonis Santvoort, a Dutch artist. Later the etching was placed in the Kupferstichkabinett in Berlin. For the translation of the inscription on the portrait the authors of this paper are indebted to Mr. Rudolf Hirsch, Director of the Union Library Catalogue, Philadelphia.

ter and waiting customers were entertained by strains of soft music from the lute or viol. The ancient and honorable right of the barber to draw blood is symbolized by the striped pole, the white band representing the bandage for the binding of wounds, and the vessel in which the pole stands, the receptacle to receive the blood.

There is reason to believe that Glauber's father attained to the profession of barber-surgeon by a marriage of convenience. Professional privileges were closely guarded, and it was not uncommon for a junior member of the guild to marry the master's widow if he could so improve his fortune. If the lady was advanced in years, the sooner he might be free to marry a younger woman. To Margaretha Fischer, widow of a barber, Glauber senior was married at Karlstadt on September 23, 1586. Nine years later he married Gertrant Gosenberger, and from the second union Johann Rudolf Glauber was born. When the boy was fifteen years of age, his father died. The keen interest shown by the younger Glauber in medicinal remedies in later years may have been due in part to his early environment.

Upon the death of his father Glauber left home and began the wandering life which he was destined to pursue throughout a restless and chequered career. Lacking formal educational training he followed the example of Paracelsus, who wrote:

> "It was the book of Nature, written by the finger of God, which I studied—not those of the scribblers, for each scribbler writes down the rubbish that may be found in his head, and who can sift the true from the false? . . . . He who wants to study the book of Nature must wander with his feet over its leaves. . . . Every part of the world represents a page in the book of Nature, and all the pages together form the book that contains her greatest revelations. . . ."

Glauber states that "he never frequented universities, nor ever had a mind to do so."[5] To those who criticized his lack of formal training he replied that "men skilled in natural things" should not be condemned or "secretly back-bitten" because they had not attained the "empty vain title of Doctor in the Universities." Other scholars sought wealthy patrons, but Glauber said he was unwilling "to live on the costs of great men, but have with my own hands gotten me my Food and Raiment. . . .

> "Let him not anothers be
> Who can of himself live free."

He perused the works of Paracelsus whom he revered as a master, and consorted with the tutored and untutored in his travels in Salzburg, Vienna, Cologne, Basel, and Frankfort. He studied the classics and the works of the ancient philosophers but perhaps was too disdainful of the work of his contemporaries. Science, which had not advanced much since Paracelsus, became to Glauber a religion.

At the age of twenty-one we find Johann Rudolf in Vienna where he earned a living by making mirrors. Here he was stricken with a "burning Feaver, known by the name of the Hungarian Disease which seldom any stranger escapes." Weak and miserable, he managed to travel about eight miles from the city when he suffered a relapse. Friends advised him to go to a well, "near a certain Vineyard" and to drink of the water to recover his appetite. He gave little credit to their words, but in his despair crawled to the spring, taking with him a "great piece of bread" with little expectation of eating it. At the well he ate a crumb sopped in the water and found that "it relished me very pleasantly who before at home loathed the greatest Dainties." Thereupon he made a cup of a hollow crust of bread and drank the water which "so excited my Appetite to eat, that at length I also eat up my Cup. I asked the Inhabitants what kind of water that was? They answered, that it was water of Salt-Petre, which I believed, being then unskilled in such things, but afterwards I found the contrary." This incident proved a turning point in Glauber's career. He spent the following winter in studying the properties of the mineral spring, and the result was the discovery of what he called his *sal mirabile*. His claim for the virtues of this simple salt were fantastic. He believed that he, a youth of twenty-one, had discovered the universal solvent—the universal medicine—sought by the alchemists for centuries, and his joy knew no bounds. From this time he devoted himself to the study of alchemy and chemistry. By means of this salt he sought to dissolve metals, reduce charcoal, exalt iron into gold, and revive a half-dead tree. Eventually he cited 26 uses of the salt in medicine, 21 in the arts, and 12 in alchemy. Today crystallized sodium sulfate, discovered as a result of a case of spotted typhus in Vienna in 1625, is known as Glauber's salt.

Little is known of Glauber between the years 1626 and 1644. It is certain, however, that he was engaged in accumulating a vast store of philosophical and experimental data which formed the basis of his future publications. In 1644 he was engaged at Giessen in directing the Royal Imperial and Court Apothecary. Here he married, only to divorce his wife a year later for infidelity. In 1645 he was obliged to leave Giessen because of the war, so went to Bonn and finally to Amsterdam. Shortly thereafter he married a second time.

In 1648 the Thirty Years War ended with the Treaty of Westphalia. In the same year, at Amsterdam, Glauber gave to the world the first fruits of his labors, "*Furni Novi Philosophi*" or "New Philosophical Furnaces." Five parts appeared between 1648 and 1650 in German; the first English and Latin editions were published in 1651 (*2*). The volume was illustrated with woodcuts of furnaces and other apparatus which Glauber had invented to carry on his experiments. He informs us that he had become discouraged with the "great misery of his labours" in tending old wind furnaces, "as also in stinks," so that he entered his "Elaboratory with loathing," and he determined to bid farewell to chemistry and apply himself to "Physick and Chirurgy, in which I was alwaies happy." But in casting

[5] Quotations in this paper, attributed to Glauber, are from "The Works of John Rudolph Glauber" (*1*).

out his wares, he found some broken crucibles containing grains of gold and silver. He could not melt them in an ordinary fire, and by an unfortunate necessity he had sold his bellows. So he was led to invent his furnaces and "did no more dispair."

Chemical bibliographers pronounce Glauber's "New Philosophical Furnaces" the most remarkable book on chemistry to appear in the seventeenth century. Glauber describes the construction and use of the furnaces and records many experiments which led to the preparation of chemical and medicinal compounds. Through his exceptional talents of observation and experimentation he realized early the importance of fire.

"How can anyone that is ignorant of fire know how to work by fire? Fire discovers many things, in which you may, as in a glass see things that are hid . . . the key for the unlocking of the greatest secrets."

Through his new furnaces he obtained a more intense and uniform heat with which to unveil the secrets of nature. He made known the art of distilling spirits and oils of many metals. These included the preparation of muriatic acid by distilling a mixture of common salt, sulfate of iron, and alum, also methods for making sulfuric, nitric, and acetic acids. The dissolving of metals and the calx of metals in muriatic (hydrochloric) acid led Glauber to make studies of the properties and uses of these oils (chlorides) as valuable medicinal compounds. Particular mention might be made of his knowledge of the chlorides of gold, iron, mercury, antimony, lead, arsenic, copper, and tin. He recommended sesquichloride of iron for the treatment of cancer and oil of gold, or *aurum potable*, as a cure for drunkenness which he described as the "root of many diseases, and the gate whereby many evils enter."

In the preparation of these chlorides and other salts Glauber realized that the principles of chemical affinity were at work. He gave correct explanations for such reactions as antimony trisulfide with mercuric chloride, arsenic trisulfide with mercuric chloride, and sal ammoniac with zinc oxide. He wrote:

"Like rejoiceth with like, and there's a disagreement 'twixt unlike things. . . . Hence it is, that . . . as one Metal is of a different nature from another, that such as are alike, love each other, and such as be unlike abhor and shun each other; and when there are divers Metals in one mass, and you would separate them, it is necessary that you do it by adding such a thing as is of affinity to the more imperfect part, and is at Enmity with the perfecter part. As for examp. Sulphur is a friend of all the Metals, save Gold, and that it hates; but yet it loves (even in imperfect Metals) one better than another."

Although the chemical philosophy of Glauber followed the pattern of the alchemists and iatrochemists, nevertheless his many new contributions to chemistry are evidence of the fact that it was not his purpose "to offer a morsel chewed before" and he bade his readers to follow his example and "seek and labour incessantly."

There were times when Glauber was led astray by the dream which possessed the minds of philosophical rogues and saints for centuries—the transmutation of base metals into gold and the search for the elixir of life. The qualifications of a true alchemist, as set forth by Glauber, were exacting and perhaps explain why few, if any, of the adepts met with success.

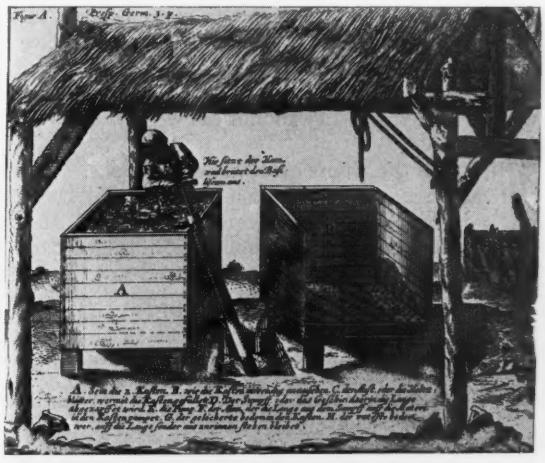
"It requires a free Man, not . . . intangled with any other humane affairs . . . at leisure continually to read good Authours, and to let no time slip wherein his labours are required. . . . Such a Man must be pious and liberal, and forward in helping the Poor; he must also be no Tattler . . . nor be prone to coveteousness. He must not be of an unconstant mind, but expect (with a patient and constant Resolution) the end . . . and he must not be presently enraged . . . if it should happen to him not to have every thing answering his expectations. He does not propose the getting of great Honours, and of having . . . power and authority. He must be furnished with the necessary means lest he be constrained through want of Coals, Materials, and other necessaries, to leave off the Work he has begun. . . . He must so lead his life as to walk unblamably before God and Man. . . . Such men are wondrous rare!"

In defense of a belief in alchemy, Glauber argued:

"Who would believe that a live bird lurkes in an egg, or an hearb having leaves, flowers and sent, in the seed? Why may not then abortive Metals, getting not yet perfection, be perfected by Art, with the help of Fire?"

He admits that scarce one of a hundred, of which he was one, did "get victuals and cloths thereby." He describes a process by which he drew forth "good gold and silver of baser metals" but warns that he cannot "promise golden mountains" as he never "made a trial in great quantity." In another passage Glauber applauds the wisdom of God in concealing from man the secret of alchemy:

"Metals remain in their impurity. And indeed God hath done well in this as in all his other works, that he hath concealed his knowledge to us: for if it were known to the coveteous, they would buy up all lead, tin, copper and iron, to turne into gold, so that rurall and poor Labourers could hardly buy metallick instruments for their use, for the scarcity; but God will not have all metals turned into gold."



PREPARATION OF SALTPETER

A and *A*—2 wooden chests; *D*—Vessel to catch the lixivium; *G*—Bottom of chest with holes; *H*—Lixivium is collected; *G*—Horse or hen dung or leaves moistened with lixivium. Age increases efficacy. Saltpeter obtained from liquor by evaporation and crystallization. The cock, according to Glauber, is engaged in hatching a basilisk!

To the alchemists posterity is indebted for certain chemical compounds useful in medicine and in industry. They lit the torch of experimental inquiry, a light destined to increase in intensity and to illuminate modern scientific research. But the secret art of alchemy remains unknown, and happily we do not sip the elixir by which we may live a thousand years.

Glauber's lot was not a happy one. Betrayed by a colleague, Christopher Farner, to whom he had imparted some chemical "secrets" and who subsequently offered them for sale as his own, Glauber became involved in a long and bitter controversy. Farner publicly deprecated Glauber's skill as a chemist and questioned his integrity. In retaliation, Glauber frustrated Farner's attempt to sell the secret remedies by publishing complete directions for their preparation.[6] The perfidious Farner was to Glauber a "double-Tongu'd Monster" who betrayed his "vanity, bragging and hellish calumny, in reprehending the industry and labour of good men." Glauber says he "ever hated Quarrelling, as more agreeable to the peevishness of Women" and would rather suffer injuries and bear losses in silence than forego his "beloved Peace." In proof of which he adds:

"So long as I have lived in the World (and I am pretty ancient) I have never been taken, by the worst of men, for a contentious person."

Glauber has been described as

"a person of easy, genteel address . . . . He spent the whole of his life in the exercise of chemistry; for the practice of which he excell'd all those of his age . . . . In his theory he was very confused; but whether in the practice he be guilty of so many falsehoods, as some have charged him with, may be much doubted: especially if we keep strictly to his experiments, without regarding the golden promises he makes" (*12*).

Glauber was accused of being something of a charlatan and mercenary in the sale of his remedies; in extenuation it must be remembered that the times in which he lived were chaotic. He had a wife and eight children to support, and lacking economic security, was driven by necessity to find the wherewithal to perform this duty.

He lacked the robust egotism of Paracelsus. He was extremely sensitive to criticism and felt that his work was not appreciated. He constantly hinted at "secrets" which he feared to publish. He lashed back at his critics as "malitious carpers" and warned them that "truth shall remaine, when haters of truth shall perish."

"I disregard the opinions of these men. It is like a wind which blows on me without overwhelming me. If Jesus Christ lived today and should perform miracles, they would destroy him. . . . Men are always the same, envious, wicked, and ungrateful.

"As for myself, faithful to the motto *Ora et Labora* I fulfill my duty as an honest man."

In his disillusionment he declared that whosoever desires that his affairs should go well should be himself both master and servant.

Like Paracelsus, Glauber made war against physicians who refused to recognize the importance of chemistry to medicine. He cautioned them in the use of newer and more powerful drugs, saying:

"Good sharpe tooles make a good workman; so good quick working and powerful medicines make a good physitian; the sharper the toole is the sooner the stone carver can spoyle his work by one cut which he doth amiss; which must also be understood of powerful medicines."

He criticized careless physicians who made use of "chymical medicines because they faine would be esteemed to know more than others, yet took greater care for their kitchens than for their patients. . . in buying ill-prepared medicines of unskilful stillers." He said that a physician should not be ashamed to make his own medicines, and added:

"If we were diligent Chymists, we need not fill Elaboratories with so many pots and boxes, nor spent so much cost in fetching . . . foreign medicinal species."

Glauber's zeal as an experimenter is shown in the following passage:

"Whilst I lay in my bed . . . afflicted with a grievous Disease. . . in the space of one Week, by the hands onely of my little Sons. . . I made three small trials or proofs . . . in a very small quantity, because by my Bed-side there was no place for doing any great Work. I am satisfied I could do much more in eight or ten Days, if God will be pleased to grant me strength for so many Days . . . ."

He predicted that others would follow him and "finde out those things which are unknown to me. For it is easier to adde to things founde out, then to finde out things unknown."

In 1651 he purchased a large stone house in Kitzingen, where he installed a laboratory. He worked on the manufacture and improvement of beer and wine by chemical means. He extracted tartar from the hitherto discarded lees of wine, receiving privileges from the Elector of Mainz, the Bishop of Wurtzburg, and the Duke of Franconia. Glauber was busy also with his *panacea antimonialis* and dispensed it to many patients, having no regard for money from either rich or poor. He composed his chief iatrochemical work "*Pharmacopoeia Spagyrica*," the first part of which was published in Nürnberg in 1654. But here also began his bitter dispute with Christopher Farner, whose calumnies contributed to Glauber's departure from Kitzingen. He journeyed to Frankfort and to Cologne, and finally settled in Amsterdam again about 1656.

Glauber's activities in Kitzingen were evidently of a profitable nature, for on his return to Amsterdam he purchased a substantial house in a good location. The laboratory which he established here was no alchemist's kitchen. A French historian, Samuel Sorbiere, visited it and described it in a letter of July 13, 1660, to Mr. De Bautru. According to him Glauber had four beautiful laboratories at the back of the house, facing a garden. In the garden he had deposited two feet of sand from the sea, and here he experimented with mineral fertilizers. He exhibited wheat which had grown to the height of one foot in six weeks, and boasted

[6] "The apology of Johann Rudolph Glauber against the lying calumnies of Christopher Farnner" (*1*).

of the power of making plants and trees grow in the most arid regions. He employed five or six men. The laboratories were spacious and the walls lined with vessels and apparatus of his own invention, and Glauber was busily engaged in filling orders. Sorbiere says that his manner was simple and sincere, that he was not embarrassed by questions, but gave logical answers, and spoke like a person of good sense.

In 1660 Glauber published "Teutschlands Wohlfahrt," in which he appealed to his countrymen to develop the natural resources of Germany and so become economically independent of other European countries. He described methods whereby wine, wood, corn, and other vegetables produced in years of plenty might be concentrated and preserved for use in lean years; methods for the reclamation of barren land, and easier and more profitable ways of extracting saltpeter, as well as processes by which minerals "may be concentrated... into metallick, or better bodies." He urged the placing of children as apprentices to artisans that they might be taught useful arts and trades; he considered the employment situation, and asked:

"Is there not sufficient store of idle fellows, whom it would be very expedient to invite to labour or (if they shun work) to banish them the Kingdom?"

He discussed means of defending the country against the Turks, but deplored warlike aggressions, saying:

"Why should we not leave India to the Indians, and have regard to our own Europe, which abundantly affordeth whatever we need for the sustenation of life?"

He points out that

"Germany is particularly highly endowed by God with all kind of mines . . . wanting only experienced people who know how to develop them properly. . . . Why are we so stupid as to send our copper to France or Spain, and lead to Holland or Venice, to be made into Spanish green and white lead that we afterwards buy from them at an increased cost? Are not our wood, sand and ashes in Germany good enough to make crystal glass, like that in Venice or France?"

He wrote:

"He that hath Eys, let him look about and use them . . . for the time comes . . . in which knowledge will be a profitable thing . . . better than a store of Goods."

In his plan for making Germany self-sustaining Glauber concludes:

"So then, when we have Food and Drink necessary for a livelyhood, and Salt-Nitre to defend us against our Enemies, and Medicines serving for the preservation of us in Health, there remains nothing else we can desire, save a little Gold and Silver, by which we may exercise Trade, and furnish ourselves with Outlandish Wares. . . ."

But he adds that the world will be deceived,

"looking after gay things, disrespecting and despising mean things, when all good things, yea, even God himself doth rejoice in simplicity. But . . . man is so blinded, that though he know not good when set before his eyes, yet he is studious of evil."

Glauber's ideas on chemical engineering and political economy were far in advance of his time. His contemporaries looked upon him as a visionary and a charlatan. He found comfort in the philosophy:

"I have indeed not buried in the Earth my five Talents graciously granted to me by God, but have put them in the publick Bank. What if the mad and blind World will neither see nor hear, it may for all of me follow its own desperate humour. . . . Let him that will, receive what I have said, for rare things and new things are not always accepted, especially being obscure: but I hope for the approbation of the age to come."

Glauber did not escape the superstition of his age, as is evidenced in his discussion of gunpowder:

"None can deny that there is no nimbler poyson than this gunpowder. It is written of the Basiliske, that he killeth man only by his look, which a man may avoyd, and there are but few (if any at all) of them found: but this poyson is now prepared and found everywhere."

He experimented on "wonderful and hitherto unknown Artificial Fires. . . and Fiery Globes (or Granadoes) . . . one pound thereof to exceed the violence of twenty pounds of gunpowder." Because of his love of peace, Glauber published his results with reluctance but excused himself with the age-old plea:

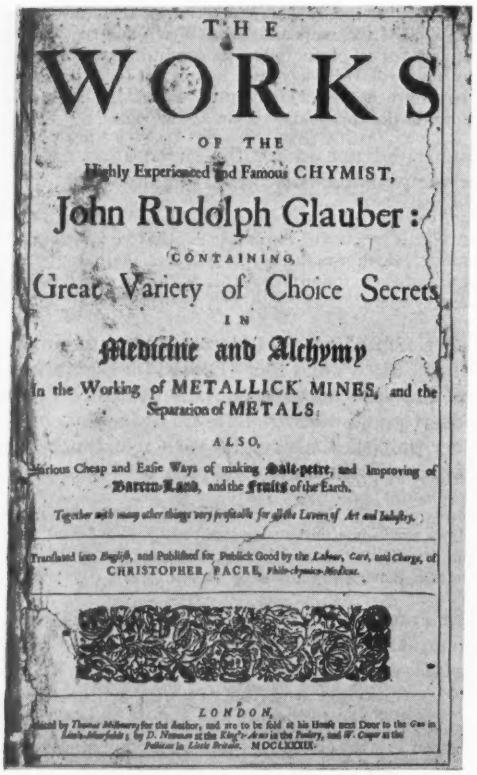
"If any new Foreign Enemies should invade our most dear Country (which is a danger we seem not far off from) we might be able to receive them with like Arms and Weapons, and by a just defence drive away any such Calamity."

Like Paracelsus Glauber wrote most of his works in German, although the titles are generally in Latin. His style was much clearer than that of Paracelsus. Between thirty-six and forty works are attributed to him. Many of his discoveries formed source material for seventeenth century pharmacopoeias. He anticipated the use of vapor and gaseous baths in medical therapy. Other valuable contributions by Glauber were his methods of making glass, the imitation of precious stones by means of colored glass, the preparation of lutes for glass vessels, the construction of crucibles, and the vitrification of earthen vessels. Glauber was keenly interested in metallurgy. He was familiar with the works of Agricola and Ercker, and described many processes for the separation of metals. The separation of lead from silver, silver from bismuth, copper from silver, the extraction of gold and silver from alloys without cupellation, and the use of niter in such separations are described by him.

Glauber was a pioneer experimental chemist. Paracelsus, Agricola, and van Helmont had recognized the method, but Glauber applied it in a practical manner to the solution of problems in agriculture, metallurgy, industry, and medicine. His work preceded that of Robert Boyle, who is generally regarded as the father of experimental chemistry.

Glauber's collected works, including "New Philosophical Furnaces," "The Prosperity of Germany," as well as his mineralogical and pharmaceutical contributions, were published in Latin in 1658, and translated into English by Christopher Packe in 1689. Glauber followed the custom of many of his contemporaries of interpolating in his scientific text bits of

moral philosophy, embroidered with accounts of personal triumphs and failures. Such digressions serve to reveal intimately the personality of the author, and it is chiefly from this source that the life story of Glauber is derived.



THE
WORKS
OF THE
Highly Experienced and Famous CHYMIST,
John Rudolph Glauber:
CONTAINING
Great Variety of Choice Secrets
IN
Medicine and Alchymy
In the Working of METALLICK MINES, and the Separation of METALS.
ALSO,
Various Cheap and Easie Ways of making Salt-petre, and Improving of Barren-Land, and the Fruits of the Earth.
Together with many other things very profitable for all the Lovers of Art and Industry.
Translated into English, and Published for Publick Good by the Labour, Care, and Charge, of CHRISTOPHER PACKE, Philo-chymico-Medicus.
LONDON,
Printed by Thomas Milbourn for the Author, and are to be sold at his House next Door to the Gun in Ludgate-street; by D. Newman at the King's-Arms in the Poultry, and W. Cooper at the Pelican in Little Britain. MDCLXXXIX.

TITLE PAGE OF GLAUBER'S COLLECTED WORKS AS TRANSLATED BY CHRISTOPHER PACKE, 1689
The names of Robert Boyle and William Penn are included in the list of subscribers

In the "Prosperity of Germany" Glauber refers to "Paracelsus his Prophesie, as I met with it."[7] He reprinted it and interpreted it by means of alchemical symbolism. The prophecy is of interest in the light of present world events, however much our interest may be tempered by skepticism:

"They will not leave me in my Sepulchre, but will hale me out hence, and lay me down towards the East. . . . Not long after the exit (or ruine) of the Austrian Empire . . . a Yellow Lion shall come out of the North, which shall be Persecutor of the Eagle and at length its Conquerour: He shall subject under this Empire all Europe, and a part of Asia and Affrica. . . . It shall first of all be a most troublesome work for him to chase away the Claws of the Eagle . . . but afore this comes to pass, there will arise extremely great Dissentions, and various Grudges amongst all Men in all Countries; the Inferiour will rise against the Superiour, so that there will be a great tumult. . . . There shall be kindled a great Fire which shall turn all into ashes, but the Omnipotent God will be at hand to help his own People, for there shall yet remain a small particle of Piety, which will take rooting, and encrease by little and little, and strike a terror into the plundering Robbers, and make that alive which seems to be dead. The Enemies and Persecutors of Christ, will call themselves powerful and everywhere bring in great Devastations, inso much that there will seem to be an end to our Actions. Now whilst the Enemy is placed in the very topmost pitch of fortune, the most just God will (by the help of a small company) destroy, and utterly root out (,) the Northern Lion accompanying him, together with all his Clerks. . . . Now when the praised Northern Lion hath finished his Course, and hath broken the edge of the Eagle's Claws, then shall Peace and Concord every where speedily . . . fly thereunto. . . ."

In 1661 misfortune overtook Glauber through a severe illness. He recovered sufficiently to publish a few works in 1663 but failing health confined him to bed during the last years of his life. The date of his death is given variously as 1657, 1668, and 1673, but the generally accepted date is 1670. Goosen Van Vreeswyck in "Silvere Rivier" (1684) says that he assisted in dressing Glauber for burial and that the date of his death was March 19, 1670. He was buried in the Wester Kerk at Amsterdam. To those who inquired what legacy Glauber had left his wife and children, Van Vreeswyck replied: "Did Raymond Lully, Johan Aurelius, Roger Bacon, or Paracelsus leave vast riches?" Glauber's wealth, he added, like that of his learned predecessors, is to be found in his writings.

[7] The exact source of the Prophecy seen by Glauber is not mentioned by him. According to Sudhoff (*14*) the Prophecy was circulated at first in manuscript form. It was widely printed during the Thirty Years War, the first printing being made in 1621. The words "left" or "remain in my grave" at the beginning of the Prophecy as given by Glauber, and the entire arrangement and alchemical interpretation indicate, in Sudhoff's opinion, that Glauber had access to the 1625 printing.

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Synthetic Resins and Plastics

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THE materials which nature provides—wood, stone, ivory, skins, fibers of cotton and wool, silken filaments, and even the earlier products of man's ingenuity and industry, such as glass, leather, metals, and alloys, are wholly inadequate for fabricating the many things we now consider essential to our comfort and well-being. The number of new products which can be synthesized from relatively simple raw materials grows incredibly, and the possibility of providing further new and useful substances seems almost unlimited, although sometimes carried to absurdity by the popular press.

The synthetic chemical industry has had a phenomenal growth in the United States since World War I, and this country now takes the leadership in the development and production of new species of molecules. These are designed, streamlined, and custom-tailored in our laboratories and plants. At present the most rapidly expanding branch of this industry involves the production of plastics—a general term which includes synthetic resins. This field also holds the greatest fascination for the layman as well as the chemist, for it directly provides many new products to look at, wear, and use in various ways with pleasure, pride, and no prejudice. The present abnormal demand for aluminum, stainless steel, and several other metals and alloys in defense production has restricted the use of these metals for ordinary purposes and made it necessary to find substitutes. This has provided an unusual opportunity for the application of plastics in fabricating many things previously made of metal. It is to be expected that plastics will be retained for many of these uses even after the present emergency has passed. The pressure of necessity is a most important factor in scientific and industrial progress.

WHAT IS A RESIN?

The term *resin* was originally applied to those natural organic products resulting from certain plant secretions, notably rosin, amber, and Chinese lac (or lacquer), and shellac which is exuded by an insect. These materials are usually hard, glass-like, non-crystalline solids, insoluble in water. They are capable of being melted or softened by heat, but may become less fusible upon prolonged heating. A *synthetic resin* is logically a product of resinous characteristics formed by synthesis from non-resinous organic compounds.

Synthetic resins were encountered long before their potential usefulness was recognized. Organic chemists were formerly largely occupied in preparing, purifying, and studying the properties of new compounds. Now and then their syntheses resulted in gummy masses which resisted all efforts to dissolve them or, if brought into solution, refused to crystallize. These products showed no definite melting points but merely became harder when heated until they finally decomposed at a high temperature to leave a residue of coke. Since a product of this type could not be dissolved, purified, crystallized, or readily analyzed it was thrown in the waste jar—often with the sacrifice of its container from which it could not be removed—and the experiment was considered a failure.

BAKELITE

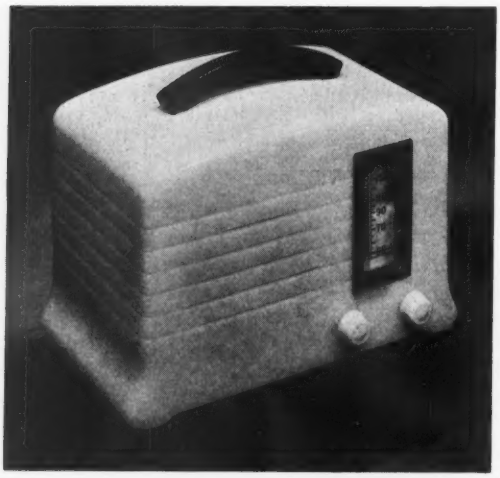
It was Dr. Leo H. Baekeland, an American chemist, who, about 1908, first saw the possibility of exploiting those very properties of resinous masses—their insolubility and infusibility—which had made them so obnoxious to organic chemists. The result, after much development, was Bakelite, the first commercially successful synthetic resin. The reactants for this resin were the relatively simple organic compounds *phenol* (carbolic acid) and *formaldehyde*. The former at that time was a by-product from coal tar, but it is now also made synthetically from benzene, which is a more abundant by-product of coke ovens. Formaldehyde is made by the catalytic oxidation of methyl alcohol, then distilled from wood (wood alcohol) but now mostly synthesized catalytically from carbon monoxide and hydrogen. The phenol and formaldehyde (in water solution) were boiled for a short time with a catalyst—ammonia or caustic soda—and a fusible resinous mass was obtained which upon the application of further heat and pressure hardened to an infusible, insoluble solid.

Courtesy of Modern Plastics

DESK LAMP AND PENHOLDER OF MOLDED BAKELITE

Thus began the intensive study, which is still in

progress, of reactions which result in the formation of resins. Thousands of these are described in chemical journals and in patents; relatively few have had real commercial success. A reference book, published in



Courtesy of Modern Plastics

RADIO OF CAST CATALIN

1935 (*1*), lists well over one thousand trade names of synthetic resins and plastic materials. As shown in that tabulation, these can be reduced to about fifteen types on the basis of chemical composition.

PLASTICS

Some of the synthetic materials which resemble resins in their methods of fabrication and uses are more properly called plastics than resins. Examples of these are the cellulose esters, such as nitrocellulose and cellulose acetate, and the cellulose ethers of which ethyl cellulose is typical. However, all synthetic resins are plastic—that is, capable of being deformed under pressure—at least at some stage in their formation. For this reason and because of the convenience of having a single name for all the products of this industry, the term plastic has recently been expanded in significance to include the synthetic resins. For example, the principal technical journals of the industry are called *Modern Plastics* (American) and *British Plastics*.

The first synthetic organic plastic of commercial importance was "celluloid"—nitrocellulose with a little camphor and alcohol. The general name for nitrocellulose plastics is pyroxylin. Celluloid was developed and first manufactured by J. W. and I. S. Hyatt in the United States in 1869. Thus it antedated Bakelite, the first commercial synthetic resin, by about forty years. It is interesting that the Hyatt brothers were attempting to invent a substitute for ivory in the manufacture of billiard balls. In this they were unsuccessful, but many uses were developed for their material. One of the first uses was for celluloid collars; later, photographic film became a major use. Pyroxylin is still a very important plastic, about twelve million pounds being produced in 1940.

The principal objection to pyroxylin in plastics is its inflammability. It has been displaced in many uses by cellulose acetate which is much less combustible. Cellulose acetate has found even wider applications for which cellulose nitrate was not adapted, especially in molded products such as automobile steering wheels, panels, and knobs; radio cabinets, chessmen, gun stocks, buttons, and costume jewelry. The production of cellulose acetate plastics in 1940 was about double that of pyroxylin. This does not include the large output of cellulose acetate in filament form for textile uses.

THE CHEMISTRY OF PLASTICS

The plastics referred to above are derived from cellulose provided by nature in cotton, wood, and other vegetation. Cellulose is a substance of high molecular complexity consisting of long chains of the unit glucose anhydride group, $C_6H_{10}O_5$. These chains are further associated into bundles to constitute the cellulose "micelle." Each of the smaller unit groups contains three hydroxyl radicals capable of reacting with acids to form esters, such as cellulose nitrate, and cellulose acetate. Or an ether, such as ethyl cellulose, may be produced through treatment of cellulose with caustic soda, followed by reaction with the proper organic chloride.

The cellulose derivatives so produced are soluble in certain organic solvents and have plastic characteristics not possessed by the original cellulose. Solutions in suitable solvents may be spun into textile filaments, drawn as sheets for transparent wrapping, or used as a surface coating. Automobile lacquers (Duco, etc.) contain nitrocellulose, resins, pigments, plasticizers, and solvents. These cellulose derivatives in granular form, with plasticizers, plus dyes and pigments for color, may be worked mechanically under heat and pressure by molding, extrusion, drawing, etc., into many useful and attractive forms. The properties of these plastics are to a considerable extent dependent upon the chemical nature of the group introduced and upon the degree of reaction. Thus when the nitration of cellulose is carried to completion by the action of a mixture of concentrated nitric and sulfuric acids the highly explosive guncotton, used in the manufacture of smokeless powder, is produced. For the production of non-explosive pyroxylin, used in celluloid and lacquers, only about two-thirds of the possible nitrate groups are introduced. In the manufacture of cellulose acetate the cellulose is highly acetylated with a mixture of acetic acid and acetic anhydride and this product is then partially hydrolyzed to produce an acetate of the desired characteristics.

Synthetic resins, in contrast with the cellulose derivatives just described, are produced by starting with small and relatively simple organic molecules. Here is a question of major chemical interest: Certain or-

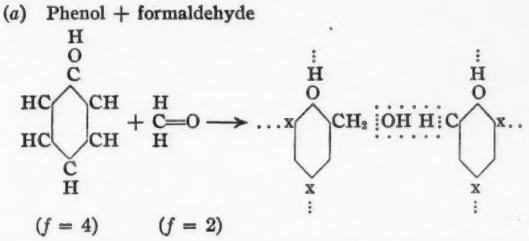
ganic chemical reactions can result in end-products which have low molecular weights and which separate from solution as crystals with sharp melting points and other clearly defined properties. Other reactions starting with equally simple molecules may produce amorphous resins of high molecular weight, which have low solubility and indefinite melting points. How can the same sort of starting materials produce such different results? The answer to this question can best be visualized with models or formulas and interpreted in terms of the *functionality* of the individual reactants (*2*). Functionality here means the number of bonds, valences, or reactive points through which one molecule may combine with another.

If a molecule of functionality *one* combines with another of functionality *one*, that is the end of the process. For example, ethyl alcohol and acetic acid each have one reactive point and react, with the elimination of water, to produce ethyl acetate. Likewise, when molecules of higher functionality (f = 2, 3, etc.) react with those of functionality one, the result is a simple end-product. However, combinations where both reacting species have functionalities of *two* or more may produce long chains (f = 2 and 2) or three-dimensional giant molecules (f = 2 and 3, etc.).

There are two principal processes by which these giant molecules are built: (1) condensation and (2) polymerization. The first involves a reaction in which small molecules, usually water, are split out in the process. In the second, nothing is lost; simple molecules of the substance ("monomer") combine due to chemical unsaturation to build larger and larger multiples of themselves called "polymers." The units which polymerize need not be identical. Often mixtures of two or more substances, each capable of polymerization, are polymerized together to obtain "co-polymers" having desirable properties. Thus most vinylite resins (*e. g.*, Vinyon) are co-polymers of vinyl chloride and vinyl acetate; several new synthetic rubbers are co-polymers—Buna S being the co-polymer of butadiene (CH_2:CHCH:CH_2) and styrene (C_6H_5CH:CH_2), Perbunan the co-polymer of butadiene and acrylonitrile (CH_2:CHCN).

(1) *Condensation* reactions in resin formation are illustrated by:

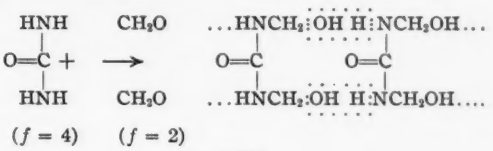
(*a*) Phenol + formaldehyde



(f = 4) (f = 2)

In the presence of an alkaline catalyst other molecules of formaldehyde may add at the points X, and the OH group of phenol is also reactive. Thus the maximum functionalities of phenol and formaldehyde are 4 and 2, respectively. The molecular structure of the resin continues to build in three dimensions as indicated by the dotted lines. If the molecular ratio formaldehyde/phenol is one or less, and an acid catalyst is used, the effective functionality of the phenol is reduced to 2 and only two-dimensional molecular chains result, constituting a fusible resin (Novolak). This fusible phenolic resin may be heated with additional formaldehyde and an alkaline catalyst, as in molding powders containing hexamethylene tetramine, to produce an infusible resin. In the manufacture of various types of resins formaldehyde is generally used as a solution in water containing about 38 per cent CH_2O. The water of this solution and that formed in the condensation reaction must be removed from the resin. This is ordinarily accomplished by vacuum distillation.

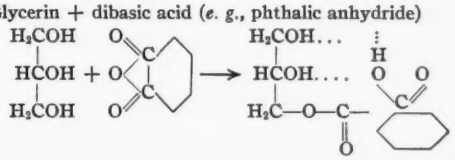
(*b*) Urea + formaldehyde



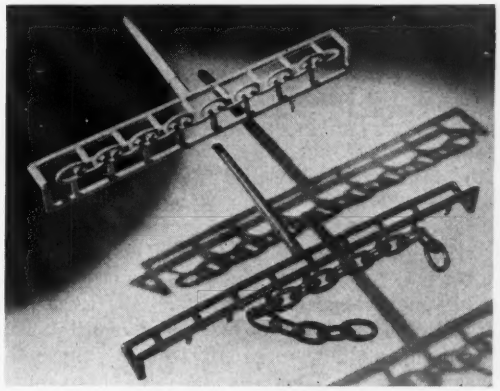
(f = 4) (f = 2)

The condensation of urea and formaldehyde is catalyzed by either acids or alkalies. The nature of the product depends upon careful control of catalyst, time, and temperature of reaction.

(*c*) Glycerin + dibasic acid (*e. g.*, phthalic anhydride)



Long-chain fatty acids from drying oils may be incorporated in the above reaction to produce *alkyd* resins for varnishes.

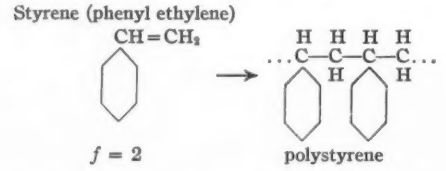


Courtesy of Modern Plastics

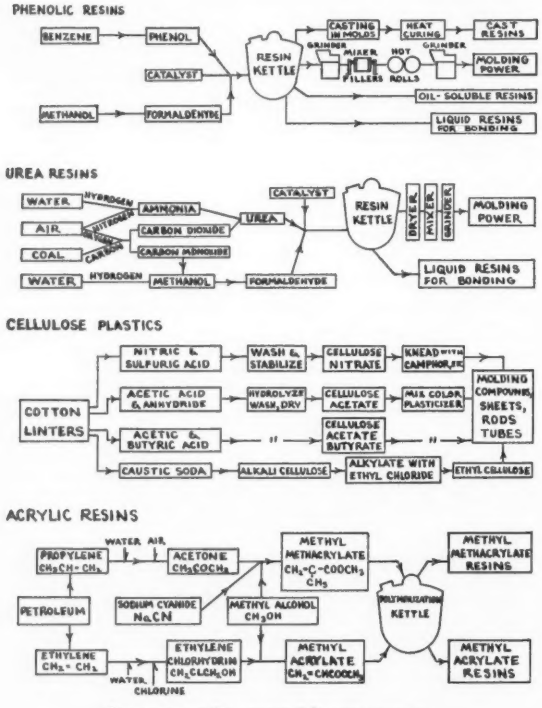
CHAIN, INJECTION MOLDED OF CELLULOSE ACETATE

(2) *Polymerization* as a mode of resin formation is characteristic of styrene, the vinyl and acrylic resins.

In these, polymerization occurs through opening the double bond or unsaturated linkage:



Styrene monomer, a colorless mobile liquid boiling at 145°C., may be polymerized by heating, or merely by long standing at room temperature, to a clear glassy solid. To produce articles of polystyrene this polymer is ordinarily granulated and molded in a hot press by compression or injection. Since the functionality of styrene is only 2, it can produce only linear polymers.



OUTLINE OF PLASTICS MANUFACTURE

This is also true of vinyl monomers—vinyl chloride (CH_2:CHCl), vinyl acetate (CH_2:$CHOCOCH_3$), vinylidene chloride (CH_2:CCl_2)—and the acrylic acid derivatives, as methyl methacrylate (CH_2:CCH_3COOCH_3). The polymers of this type are permanently fusible; they soften and flow repeatedly when subjected to heat and pressure. This behavior is in sharp contrast to that of the phenolic and urea resins which become hard and infusible when polymerized by heat subsequent to the condensation reactions.

CLASSIFICATION OF RESINS AND PLASTICS

In view of this fundamental difference in response to heat treatment, resins and plastics are logically divided into two classes: (1) *Thermosetting* or heat-convertible and (2) *Thermoplastic* or heat-nonconvertible. A third type, (3) *Element-convertible*, may be added to include such materials as rubber, which is hardened by vulcanization with sulfur, and drying oils which harden by combining with oxygen.

The more common resins and plastics are classified upon this basis in the accompanying outline. Forms and uses of these are briefly indicated and some of the trade names are listed.

SYNTHETIC RESINS AND PLASTICS
Principal Types and Uses

Thermosetting

1. Phenol-formaldehyde (Bakelite, Catalin, Durez). Molding, casting, bonding; modified (oil-soluble)—varnish.
2. Urea-formaldehyde (Beetle, Plaskon, Uformite). Molding, lamination, surface coatings, textile treatment.

Thermoplastic

1. Cellulose nitrate or pyroxylin (Celluloid, Pyralin). Sheets and rods for forming; photographic and movie film; nitrocellulose lacquers (Duco).
2. Cellulose acetate. Textile filaments (acetate rayon, Celanese, Teca); molding (Lumarith, Tenite); home movie film; transparent wrapping (Kodapak, VuePak).
3. Acrylates, methyl methacrylate (Acryloid, Crystalite, Lucite, Plexiglas). Molding, casting, bonding, coating; airplane windows and enclosures, highway reflector lenses, safety glass, dentures, textile finishes.
4. Vinyl resins—polyvinyl chloride (Koroseal), polyvinyl acetate, co-polymers (Vinylite, Vinyon). Textiles, elastic belts, etc. Vinylidine chloride (Saran). Polyvinyl acetals (Alvar, Butacite, Formvar). Coatings, bonding, safety glass.
5. Styrene (polystyrene, Loalin, Styron). Molding, electrical insulation, transparent containers and closures, refrigerator panels and trays.
6. Polyamide (Nylon). Textile filaments, bristles.
7. Protein-formaldehyde. Casein[2] (Ameroid, Gala, Galorn); molding, buttons, etc., wool substitute (Lanital). Soybean; molding compositions.

Element-convertible

1. Synthetic rubbers—elastomers (Ameripol, Buna, Neoprene). Printing rolls, hose for gasoline and oils.
2. Oxidizing oils (linseed, tung); oil modified alkyd resins for coatings (Dulux, Duraplex, Glyptal). Polymerization also occurs in "drying."

Rayon (viscose) is regenerated cellulose. Just before spinning it is cellulose xanthate—a plastic. Textile filaments, transparent wrapping (Cellophane, Sylphrap).

THE UTILIZATION OF PLASTICS

Numerous applications of synthetic resins and plastics have already been mentioned. One of the chief advantages of these materials is the variety of ways in which they may be fabricated into finished articles. In the following outline the principal methods are briefly indicated. It should be understood that any one type of resin or plastic is not adapted to every method of utilization.

1. *Casting.* Liquid resin is poured in molds, usually of lead, these are placed in curing ovens to polymerize the resin by heat, and the solidified resin is then removed from the molds. Many articles are cast in final form, but cast resins machine well, so that rods or blocks may be sawed, cut, or turned and then polished to produce finished articles. Most castings are made with phenolic or acrylic resins.

2. *Molding.* Thermosetting phenolic and urea resins in which chemical reaction (final polymerization) has not progressed to completion may be pulverized, mixed with fillers, dyes, and pigments, and molded in a hot press to produce finished articles. This step converts a thermosetting resin into the final, infusible stage.

Certain compositions with phenolic, bituminous, or inorganic binders are *cold molded* and subsequently baked. Thermoplastic materials, especially cellulose acetate, styrene, and acrylic resins, are also commonly fabricated by molding.

Injection molding is a special development of this art for thermoplastics. In this technic the plastic, softened by heat, is forced through a main channel by a piston, and into branching channels leading to the mold cavities which are relatively cooler. Thus by a single stroke of the piston a rather large object or multiple units of a smaller molded object are produced. The mold is opened, the contents removed, and the connecting material is broken away from the molded articles. Any scrap material from thermoplastic moldings can be used again. For this reason, and because the molding cycle is short and the machines largely automatic, injection molding is a very efficient method of utilizing plastics. A process called *transfer molding*, somewhat similar to injection molding, is being developed for thermosetting materials.

Extrusion or extrusion molding is also analogous to injection molding. It is a process for extended uniform shapes (rods, tubes, strips, etc.) in which a heat-softened plastic is forced through a die or orifice having the same form as the cross section of the desired article.

Courtesy of Modern Plastics

FURNITURE WOVEN OF EXTRUDED CELLULOSE ACETATE-BUTYRATE, TENITE II

3. *Bonding.* The use of plastics and resins as bonding agents, glues, and binders is expanding with great rapidity at present. Perhaps the most spectacular and revolutionary field for resins is the plywood industry (*3*). Thermosetting resins produce a bond that is stronger than the wood itself, wet or dry. The product is verminproof and quite resistant to heat. Airplane wings and fuselage may be constructed of resin-bonded plywood. Paper, cloth, or thin wood

Courtesy of Modern Plastics

RESIN-BONDED PLYWOOD, READING ROOM, CONGRESSIONAL LIBRARY

veneers, impregnated with resin, are laminated in a hot press to form sheets for electrical insulation, radio dials, table tops, refrigerator panels, and even automobile bodies. Resins are used for bonding sand cores in foundries, especially for casting brass and aluminum. Asbestos and other materials are bonded with resins to produce brake-linings and clutch-facings. Glass fiber bonded with resin is used for thermal insulation and for air filters. Mixtures of grit and thermosetting resins are molded to produce abrasive wheels; abrasives are bonded to cloth or paper by means of resins. An interesting story could be told about each development in this field but the following one is typical.

Safety Glass. The production of non-shattering glass, principally for automobile windshields and windows, by laminating thin sheets of plate glass with an interlayer of plastic is an important development in the plastics industry (*4*). While not the first to visualize safety glass, one of the early inventors in this field, Edouard Benedictus of Paris, gives this account of his conception of the idea:

"One day in 1903, as I was setting my laboratory to rights, and moving the glassware around, a bottle slipped from my hands and fell to the floor from a considerable height. This bottle, of about one-liter size, I picked up apparently unbroken. The glass was starred like Bohemian crystal but was held firmly together by some internal adhesion.

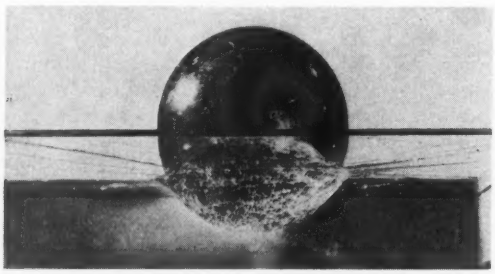
"The bottle had contained a solution of nitrocellulose, from which, over a period of fifteen years, all of the solvents had evaporated, thus lining the interior of the bottle with a celluloidal coating of great strength. So firmly were the fragments of glass held by this layer that not a single piece of any size became detached or even loosened. Having made a thorough examination of all parts of the bottle, I attached to it a label reading 'November, 1903—this flask fell from a height of 3.5 meters, was picked up in its present condition.'

"I replaced the bottle on its shelf and thought no more about it until one day when my attention had been attracted by two accidents caused by the breaking of glass in vehicles. Two young women suffered lacerations of the neck in collisions.

"I was sitting after my dinner thinking intently of these two accidents, when suddenly, without warning of any sort, there appeared upon the wall, faintly illuminated, and moving as though alive, the image of my bottle. Emerging from my reverie, I rose to my feet, entered my laboratory, and gave myself up to deliberate contemplation of the possibilities of this embryo of an idea which had come to me from my bottle. At dawn the next morning I found myself still with the bottle in my hand, not having stirred for nine hours, but with a program of experimentation drawn up, which I proceeded to carry out step by step.

"By the next evening, with the aid of a letterpress, I had prepared the first sheet of Triplex glass, complete in all its characteristics and its promise for the future."

Pyroxylin (nitrocellulose) plastic for safety glass had the objectionable features of discoloration by sunlight, of becoming cloudy or hazy, and of decrease in toughness and cohesion at winter temperatures. Cellulose acetate offered some improved characteristics and by 1939 had almost completely displaced pyroxylin in the manufacture of safety glass. More recently cellulose acetate has in turn been largely displaced from this use by the polyvinyl acetal resins. These are prepared by polymerizing a vinyl compound, usually vinyl acetate, hydrolyzing this product to polyvinyl alcohol, and condensing this with an aldehyde.

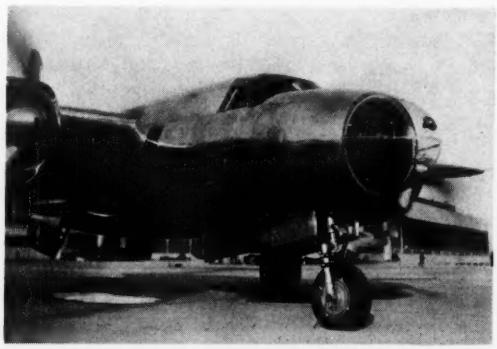


Courtesy of Modern Plastics

BALL DROPPED ON PANE OF POLYVINYL ACETAL SAFETY GLASS

4. *Coating.* The use of phenolic, alkyd, urea, and other types of resins in various combinations for protective coatings represents a very important and growing application of these materials. Such coatings are generally very durable, resisting the destructive effects of moisture, sunlight, and heat.

Ordinary phenol, C_6H_5OH, is only the first member of the extensive class of phenols which in general react with formaldehyde or other aldehydes, under the influence of a suitable catalyst, to produce resins. Resins made from certain substituted phenols are oil-soluble and are therefore used in conjunction with drying oils to produce oleoresinous varnishes and baking enamels (*5*).



Courtesy of Modern Plastics

MARTIN B-26 BOMBER WITH PLEXIGLAS ENCLOSURES

Textiles may be treated with resins to increase body and stiffness, to impart resistance to creasing and wrinkling, or to produce novel effects in appearance.

Polyvinyl acetals are used to coat wires or other surfaces for electrical insulation. Vinyl resin linings are used in metal containers and closures for many food, drug, and cosmetic products. Even steel barrels and tank cars may be protected against corrosive contents by these resins.

The foregoing survey of plastics and their uses is necessarily incomplete. It must be emphasized that the field is growing very rapidly by the addition of new materials, the improvement of older ones, and the development of new applications. Any publication on the subject will need additions and revisions by the time it reaches the reader. The purpose of this one will have been served if it provides a better understanding of the things yet to come in this plastic age.

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(1) ELLIS, "The chemistry of synthetic resins," Reinhold Publishing Corp., New York City, **1935**.
(2) KIENLE, "Observations as to the formation of synthetic resins," *Ind. Eng. Chem.*, **22**, 590 (1930).
(3) "Resin-bonded plywood," *Modern Plastics Catalog*, 1941, p. 414.
(4) RANDOLPH, "Evolution of safety glass," *Modern Plastics*, **18**, 31 (June, 1941).
(5) TURKINGTON AND ALLEN, "Oil-soluble phenolic resins," *Ind. Eng. Chem.*, **33**, 966 (1941).

CORRECTION

A CORRECTION for "Heavy Water," in the November, 1941, issue, page 515: "Instead of weighing 62 pounds per gallon as does ordinary water, this residue of water in the container gradually increases in specific gravity until ultimately it weighs over 68 pounds per gallon," should read "62 pounds per *cubic foot*," and "68 pounds per *cubic foot*."

The Iodoform Reaction by Methods of Microscopy

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SOME technicians have frequent occasion to detect the presence of ethanol, acetone, or certain other compounds by resorting to the use of the well-known iodoform reaction. As a rule considerable time could be saved by adapting this test to the methods of microscopy. A further advantage of such an adaptation is the fact that a very minute quantity of sample will suffice.

When the customary procedure is applied to colored solutions which contain only small concentrations of the compound sought, the iodoform precipitate may be so faint as to cast doubt upon the interpretation of results. On the other hand, since the microscopic test depends upon the formation of characteristic crystals, visual identification of any iodoform produced, even in a colored solution, is conclusive.

It has been claimed inadvisable to perform the test on a microscope slide because of the volatility of the iodoform.[1, 2]

However, by introducing certain modifications, including the use of a hanging drop slide, the test has proved quite satisfactory even with solutions containing less than one per cent of ethanol or its equivalent.

To perform the iodoform reaction under the microscope the following should be provided.

1. A hanging drop slide having a concavity 1.75 mm. deep.
2. An ordinary microscope slide.
3. A flat-topped steam hot plate. This may be a simple type such as shown in Figure 1.

FIGURE 1.—SIMPLIFIED STEAM HOT PLATE, SHOWING RELATIVE POSITIONS OF THE HANGING DROP SLIDE AND THE COVER SLIDE. (THE STEAM HOT PLATE CONSISTS MERELY OF A 250-ML. BEAKER PROVIDED WITH A "TIN CAN" LID)

4. Capillary pipets, drawn from 5- or 6-mm. glass tubing. These are so made that the outside diameter of the lower end measures just about 1.5 mm.
5. A cooling block.

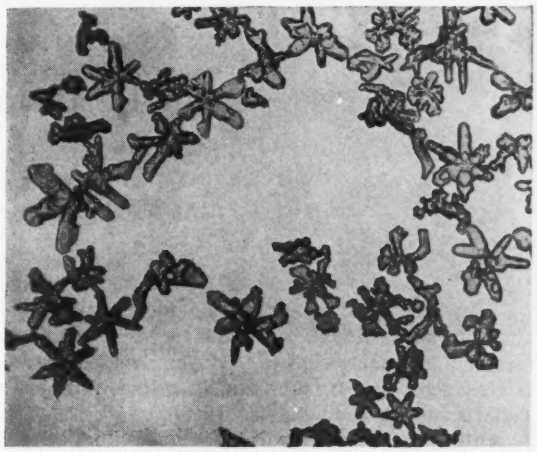

FIGURE 2.—TYPICAL GROUP OF IODOFORM CRYSTALS AS FOUND ON THE COVER SLIDE. (ABOUT 235×)

The sample consists of only two small drops as delivered from one of the capillary pipets. The latter are filled by capillary action rather than by suction. Holding the pipet in a nearly horizontal position, the tip is applied to the surface of the liquid. The amount which flows into the tube can be readily controlled by varying the angle of inclination. A finger placed over the mouth of the pipet retains the liquid until released. When the finger is removed not all of the liquid flows out of the pipet, even when the latter is in a vertical position. After a bit of practice, however, the analyst will be able to ascertain the correct amount of sample to take into the capillary in order that the desired two-drop sample may be delivered.

To the sample on the reaction slide a pinch of anhydrous sodium carbonate is added. A very convenient spatula for taking up an appropriate amount of the carbonate is made by flattening the end of a short length of 20-gage platinum wire.

In order partly to disperse the sodium carbonate in the liquid the slide is rotated, after which there are added, from a micropipet, two drops of a solution of iodine in potassium iodide. This reagent should be about 0.2 *N*. At this stage it is important that none of the reactants be permitted to spread to the plane surface of the hanging drop slide.

[1] FOULKE AND SCHNEIDER, "Microtechnique of organic qualitative analysis," *Ind. Eng. Chem., Anal. Ed.*, **12**, 555 (1941).

[2] EMICH-SCHNEIDER, "Microchemical laboratory manual," John Wiley and Sons, Inc., New York City, **1932**, p. 119.

To prevent loss of the liquid by evaporation an ordinary microslide is placed over the reaction mixture in such manner as to leave a small opening to serve as a vent. (Figure 1.) The combination is then carefully transferred to the hot plate. The water in the latter should be boiling vigorously.

After three minutes the slides are removed to a cooling block. In the absence of a regulation cooling block a pile of glass plates may be used for the purpose.

After a short interval to allow the mixture to cool, the upper slide is carefully lifted from the reaction slide and inverted. This cover slide is then examined for microscopic crystals of iodoform which may have sublimed from the reaction mixture. As a rule the crystals resemble six-pointed "snow stars" but occasionally they may appear as thin hexagonal plates. While it is true that the crystals are frequently imperfect, they can always be identified as belonging to the hexagonal system. A typical group is shown in Figure 2. If none of the iodoform has sublimed to the cover slide the crystals can be found in the residual reaction mixture on the hanging drop slide.

Students in chemical microscopy who have applied the foregoing procedure to "unknowns" containing not over two per cent of an appropriate organic ingredient have found it fully as reliable as most qualitative tests, even when working under the stress of a "practical" final examination.

STOICHIOMETRIC CALCULATIONS ON THE BASIS OF CRYSTAL LATTICES[1]

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IN A paper on "The Silica-Alumina Relationship in Glass,"[2] Safford and Silverman have shown that aluminum may enter the crystal lattice in fourfold coördination, replacing silicon. Boron, phosphorus, and other elements may be substituted for silicon similarly. In quartz and other minerals, silicon atoms are usually at the centers of tetrahedra with an oxygen atom at each of the four corners. The specialist in X-ray studies of crystal structure may refer to the "silicon ion" and the "oxide ion." Whether the silicon or its substituted aluminum unit is an atom or an ion, one atomic weight of silicon is displaced by one atomic weight of aluminum and, therefore, the old stoichiometric calculations based on the common valences of the respective elements should be abandoned in such cases. Alumina in the white sapphire is in sixfold coördination and has the normal valence of three, but in glasses and certain minerals it may have fourfold coördination. Structure of substances determines the kind of substitution-calculation which should be made, and the chemist should broaden his interpretation by including structure studies.

In a glass the SiO_4 tetrahedra are not arranged as in crystals, but there is a random scattering of these tetrahedra, with holes here and there into which sodium ions or calcium ions may slip as in the production of a soda-lime glass. Now, suppose that an aluminum atom replaces a silicon atom in one tetrahedron. The replacement is atom for atom, or ion for ion in the terms of the X-ray specialist. Although the substitution is atomic (26.97 parts by weight of aluminum for 28.06 parts by weight of silicon), a normally trivalent ion has replaced a tetravalent one in the lattice. If a sodium ion was located in one adjacent hole and a calcium ion in another, it is now possible to substitute a second calcium ion for the sodium ion to make up for the unit of valence lost by the displaced silicon ion. In other words, while the substitution in one spot may be atom for atom and not equivalent, the total valence of the system remains unaltered. Although not of particular interest to the average chemist, the example cited accounts for the possibility of producing higher lime-containing soda-lime glasses, when some alumina is substituted for silica in the glass batch, or mixture of raw materials.

Isomorphous substitution, independent of valence, is not new to the chemist. He knows that arsenic, a Group V element, may replace sulfur, a Group VI element, in sulfides. Perhaps he is less familiar with some mineralogical facts which X-ray studies have cleared. Let us consider the mineral albite (soda feldspar), known to most of us by the formula $NaAlSi_3O_8$, and rewrite this $Na.Si(AlSi_2O_8)$. By substituting one aluminum for one silicon (valence change 4 to 3), we can replace the sodium by a calcium (valence change 1 to 2) and get $CaAl(AlSi_2O_8)$, better known as anorthite with the formula $CaAl_2Si_2O_8$. Similar changes may be effected in potash feldspar by replacing potassium by barium when an aluminum atom replaces a silicon.[3]

It is not the purpose of this paper to furnish an elaborate treatise. A principle is presented. Interested chemists can find numerous examples of "substituted" minerals in the literature on mineralogy and the atomic structure of minerals.

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[1] Contribution No. 441 from the Department of Chemistry, University of Pittsburgh. Paper presented before the Division of Chemical Education at the 102nd meeting of the A. C. S., Atlantic City, New Jersey, September 11, 1941.

[2] Paper presented before the Glass Division, American Ceramic Society, Conneaut, Pennsylvania, September 13, 1941.

[3] BRAGG, "Atomic structure of minerals," Cornell University Press, Ithaca, N. Y., 1937, p. 230.

Edwin Emery Slosson: A Chemist of the West[1]

DOROTHY BARTON

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IN THIS age scientific discoveries and inventions come rapidly. But ignorance on the part of the general literate public concerning these matters sometimes makes the going difficult for the researchers and workers in the field of science. In order to have a well-balanced program science must have as well as its research workers those who are capable of clarifying and humanizing the knowledge brought to light in laboratories. There must be a group of men who are willing to take the time to make the man on the street understand the mysteries of science so that he can adapt himself to an ever changing world. It is very difficult to popularize abstract truths and any person who succeeds in the task must of necessity be gifted. He must first of all grasp the full significance of the facts himself and then must be careful not to distort them in order to make the common mind appreciate and understand them. Such a person was Dr. Edwin Emery Slosson.

Very often when Edwin E. Slosson's name is mentioned it is as a former member of the staff of *The Independent* magazine in New York. And he is frequently cited as the director of the Science Service in Washington, D. C., up to the time of his death. But important positions of that nature demanded a vast knowledge and some experience in the field of science. Slosson's fundamental knowledge of chemistry and science in general was obtained in the West, although sometimes that fact is overlooked. His contributions to chemistry while residing in Kansas and Wyoming and while doing graduate work at the University of Chicago prepared him for his work in the East.

His father, William B. Slosson, lived originally in New York, but in 1857, at the age of 21, his adventurous spirit prompted him to become one of the first settlers of Kansas. Here he made a home and established the first store in Albany. His job was a difficult one because he had to haul his goods for the store 60 miles by ox team from the Missouri River at St. Joseph, Missouri. It was at Albany, Kansas, that Edwin Slosson was born on June 7, 1865. His mother, Louise Lilly Slosson, had been a school teacher in New York prior to moving West. She taught her son many valuable lessons, among them an appreciation and love of books.

After Edwin Slosson had finished his grammar-school education he attended the Leavenworth (Kansas) High School. Then he took up his studies at the University of Kansas at Lawrence. He was much interested in science, specializing in chemistry. However, his interests were diversified and his work at the University was evidently well done, since he was elected to both the literary and the scientific honorary societies. He was a member of Phi Beta Kappa and Sigma Xi. In 1890 he obtained his B.S. degree and took some graduate work at the University.

DR. EDWIN E. SLOSSON IN THE LECTURE ROOM, TEACHING CHEMISTRY AT THE UNIVERSITY OF WYOMING IN THE FALL OF 1897

Then he was faced with a serious problem indeed—the age-old one that confronts a large percentage of graduates every year. Although he had applied at several different places, a job did not seem to be immediately forthcoming. Finally he took temporary work as a member of a paleontological expedition at a solitary spot in Kansas. Then, by coincidence, in one day he received two offers of positions. One came from a large university on the Atlantic coast, the other from the small University of Wyoming. It was not only a choice of residence but the choice of a career. The offer from the Atlantic coast was for work in the field of psychology, whereas the one from Wyoming was for the position of Assistant in Chemistry. After a short time he made his decision.

So in 1891 Slosson was called to the University of Wyoming at Laramie, where he had charge of teaching chemistry and chemical research at the Wyoming Agricultural Experiment Station. In addition to this he accepted another responsibility of a different type. On August 12, 1891, he married May Preston of Centralia, Kansas, a young woman who was outstanding as the first woman to get a Ph.D. degree at Cornell University.

The work at the Experiment Station was determined largely by the nature of the land of the state. Attention was concentrated on the study of aridity. In contending with aridity there were two difficulties, the supply of sufficient water and the dispersing of the ac-

[1] Presented before the Division of the History of Chemistry at the 101st meeting of the A. C. S., St. Louis, Missouri, April 8, 1941.

cumulated soluble salts known as alkali. Most of the salts of Wyoming consisted of Na_2SO_4, $MgSO_4$, and NaCl in varying proportions. Slosson studied the effect of salt solutions on germinating seeds. In many

EXPERIMENT STATION COUNCIL AT LARAMIE, WYOMING, MARCH, 1893. (E. E. SLOSSON IS IN THE BACK ROW, AT THE LEFT)

cases he found that there was no excess of alkali on the surface of the soil, but there might be beds of it several feet below. In the bulletins of the Experiment Station he published many observations on the origin, constitution, and distribution of alkali in Wyoming. He tried to find some means to retard or diminish the accumulation of alkali and to redeem the soils that were so alkaline as to be of little agricultural importance.

Another phase of chemistry that Slosson worked on at the Experiment Station was that of petroleum oil. All this work was to help him a great deal later when he wrote his well-known book of "Creative Chemistry" and articles on petroleum products, coal-tar dyes, etc. He studied the heating power of Wyoming coal and oil. He published many items in the bulletins of the Experiment Station on the geology of the gypsite deposits of Laramie, the chemistry and the manufacture of cement plaster at Laramie, the effect of sand on the crushing strength, and certain retarders and accelerators. His series of papers on petroleum was also extensive.

Much activity centered around the agricultural school. In 1893 the University entered a grass exhibit at the World's Fair in Chicago and received a medal for it. Slosson acted as a special demonstrator in chemistry at the Fair.

But his work at the Experiment Station was only part of his job. The other half consisted of teaching chemistry classes of the University students. The president of the University was a great advocate of University extension courses in the state. After a speech of his in 1892 some twenty-four Laramie citizens signed up for a course and as first choice elected to take chemistry under Slosson. This must surely have affected his work later on as a popularizer of chemistry.

In the following terms at the University of Wyoming some new courses were introduced. It is to be noted that Slosson handled a course in experimental psychology. He evidently did good work in that field too, for he became noted in the community as a teacher of psychology, having established laboratory practice in the school. This was another indication of his wide diversity of interests.

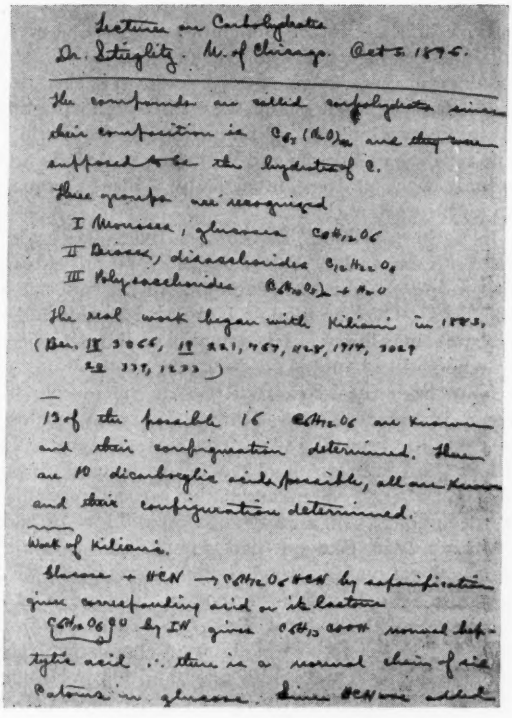
The University at that time had no regular summer school, but it is reported that Slosson taught a few students of chemistry in the summers of 1897–99.

Another student activity of that time was the Camera Club. Dr. Slosson was interested in the subject and lectured on photography in Laramie and Cheyenne.

His sense of humor was noted on the campus. It must have helped him a great deal when faced with disciplinary problems. And apparently he was fond of writing poetry. That fondness, combined with his great sense of humor, often entertained his students. However, he was known as a very thorough teacher of chemistry and one who demanded much of those who worked under him.

Another side of the picture is presented when we see Slosson in the role of a preacher. As a professor he was called upon many times to give talks in the chapel and he occupied the pulpit a number of times when the regular minister could not fulfil the appointment himself. Later (1925) he published a collection of some of the sermons and talks he had delivered, entitled "Sermons of a Chemist."

Because his wife had a Ph.D. degree and he himself



Lectures on Carbohydrates
Dr. Stieglitz. U. of Chicago. Oct 5. 1896.

The compounds are called carbohydrates since their composition is $C_6(H_2O)_n$ and they were supposed to be the hydrates of C.

Three groups are recognized
I Monoses, glucoses $C_6H_{12}O_6$
II Bioses, disaccharides $C_{12}H_{22}O_{11}$
III Polysaccharides $(C_6H_{10}O_5)_n + H_2O$

The real work began with Kiliani in 1885,
(Ber. IX 3066, 19 221, 767, 1128, 1914, 3029
22 339, 1233)

13 of the possible 16 $C_6H_{12}O_6$ are known and their configuration determined. There are 10 dicarboxylic acids possible, all are known and their configuration determined.

Work of Kiliani.

Glucose + HCN → $C_6H_{12}O_6$HCN by saponification gives corresponding acid or its lactone

$C_6H_{12}O_6$ 90 by HI gives $C_6H_{13}COOH$ normal heptylic acid ∴ there is a normal chain of six C atoms in glucose. Since HCN was added

PAGE FROM SLOSSON'S NOTES ON A LECTURE BY DR. STIEGLITZ ON ORGANIC CHEMISTRY AT THE UNIVERSITY OF CHICAGO FOR OCTOBER 5, 1896

had only an M.S. degree from the University of Kansas, Slosson decided that such a state of affairs was not to his liking and spent his summers working at the University of Chicago, under Professors John Nef and Stieglitz. Examination of his notebooks, left to the University of Wyoming, shows good organization of material. His notes were neat and legible—certainly a credit to any student. Some of his notebooks on organic chemistry, nitrogen compounds, and terpenes have been preserved by the Library of the University of Wyoming. For his thesis he submitted a dissertation on "Acylhalogenamine Derivatives and the Beckmann Rearrangement."

After finishing the hard, driving work on his degree he was ready for a summer vacation. He wrote to Hamilton Holt, the editor of *The Independent*, and asked if he would not like an assistant for the summer—someone who would give his service in return for board and a railroad ticket to New York. Mr. Holt agreed and Dr. Slosson did the odd jobs of editors who were taking their vacations. When the fall months came he returned to his old position in the chemical laboratory of Wyoming. But in December he received a telegram from Holt offering him the position of Literary Editor of *The Independent*. In the early part of 1904 Edwin Slosson definitely severed connections with the University of Wyoming and went to take up his position in New York. He remained on the staff until 1921. He made his scientific articles very interesting and entertaining, and that appealed to the public.

In 1921 an institution for the popularization of science, namely Science Service, was established in Washington, D. C., and Slosson was asked to be its director. He accepted and spent the rest of the years remaining to him in popularizing scientific information by radio, lectures, newspapers, magazines, and books. He finished his job on October 15, 1929, and the world mourned the passing of a scientist.

Possibly the best known book that Slosson wrote was the one entitled "Creative Chemistry," which is a collection of articles prepared for *The Independent*. These had been written primarily for the purpose of acquainting the general reader with the recent achievements of industrial chemistry. "Creative Chemistry" still serves as a supplementary reading book for chemistry in many high schools and colleges.

DR. SLOSSON (SECOND FROM THE FRONT IN ROW AT RIGHT CENTER) INSTRUCTING IN THE CHEMISTRY LABORATORY AT THE UNIVERSITY OF WYOMING (CLASS OF 1897–98)

Among his other works are " Great American Universities," "Major Prophets of Today," "Six Major Prophets," "Snapshots of Science," "Easy Lessons in Einstein," "Keeping Up with Science," and "The Synthetic Kingdom." He also contributed a large number of articles to *Collier's Weekly*.

Edwin Emery Slosson was a composite of literary man, scientist, and humanist. He had a good background of scientific knowledge and used his literary ability to good advantage in giving the facts to the public. His work in New York and Washington, D. C., was the culmination of his efforts in the West.

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Origin and Transformation of Carbohydrates in Plants[1]

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TO THE extent that one can speak at all of a beginning of so large and complex a subject as organic chemistry, from the biochemist's viewpoint at least, such a beginning is provided by the great group of carbohydrates. The traditional arrangement of organic compounds, beginning with the hydrocarbons and developing with groups attached to the carbon atoms of a chain, is clearly a convenience for pedagogic and classification purposes. It obviously is not a system of classification which has any bearing on the origin or the sequence of appearance of these compounds in the great laboratory of organic nature. The biochemist has considered the compound of first importance in this respect to be a carbohydrate. In accordance with this conception all the carbon compounds which appear in nature have arisen, directly or indirectly, from this mother substance.

This is at least the concept which has been generally entertained since the time of Emil Fischer's classical researches on the carbohydrates. In this opinion Fischer had apparently been strongly influenced by the conclusions of Sachs and others of his countrymen and notably by the publications of Brown and Morris in England. From this point of view, therefore, sugar is the mother substance of all life and of all the carbon compounds which appear in nature.

A conclusion of such basic significance for an understanding of the chemistry of life processes should be subjected to the severest scrutiny. For the consequences of this dictum influence not only our entire concept of the manner in which carbohydrates are manufactured by the plant, but also affect many of our ideas of plant and animal nutrition.

Let us examine, therefore, briefly what is the basis of this conclusion that a carbohydrate is the primary product of photosynthesis. It is based, first of all, on the measurement of what is termed the photosynthetic quotient; that is, the ratio of the volume of carbon dioxide absorbed to the volume of oxygen liberated during photosynthesis, CO_2/O_2. This quotient gives an indication of the degree to which the carbon dioxide has been reduced in a reaction in which water is assumed to be the hydrogen donor. For example, if the carbon dioxide were reduced to oxalic acid the quotient would be 4, if it were reduced to formic acid it would be 2, to glycollic acid 1.33, and if it were reduced to a compound of the general formula $C_nH_{2n}O_n$ (that is, a carbohydrate), it would be 1. If substances were produced of a higher state of reduction, such as fats or hydrocarbons, the value of the ratio would, of course, be less than unity. It hardly needs special emphasis that the value of this ratio gives no evidence of the exact compound which is formed in photosynthesis, as has been occasionally assumed; it simply indicates the type of compound, *i. e.*, the degree to which the carbon dioxide has been reduced in this reaction.

This question of the photosynthetic quotient has been extensively investigated. Early experiments yielded a value for the quotient of close to unity. It should be stressed that this value was based upon observations made after the plant had been subjected to illumination for some time, that is, after the photosynthetic process was well under way. This value of unity for the photosynthetic quotient has been accepted as evidence that carbohydrate is the major product of the photosynthetic reaction.

It now appears, however, that this conclusion may be open to some doubt. This uncertainty arises from the fact that the observed values of the photosynthetic quotient are variable. While it is true that the photosynthetic quotient is very close to unity after an extended period of illumination, it requires some time to

[1] Presented before the Division of Sugar Chemistry and Technology, in the Semicentennial Commemoration of Fischer's Publication of the Structure of the Hexoses, at the 101st meeting of the A. C. S., St. Louis, Missouri, April 10, 1941.

attain this value. During the first minutes of illumination the ratio of carbon dioxide absorbed to oxygen liberated varies considerably from unity. The interpretation of these changing values of the quotient during the initiation of the photosynthetic processes is one of the most disputed problems in the subject at the present time, and we cannot enter into this discussion here. Suffice it to point out that our concept of the process has been materially altered as a consequence. We cannot regard it as a simple reaction:

$$xCO_2 + H_2O \rightarrow 1/x\,(CH_2O)_x + O_2$$

as is so conveniently written in the textbooks. Of this we are quite certain.

The process is composed of a series of apparently integrated reactions, some of which are true photochemical reactions proceeding instantaneously, with a low temperature coefficient; others are dark reactions, proceeding more slowly, catalytic in nature, and with a normal temperature coefficient.

These reactions succeed each other so rapidly that intermediate products formed in any one of them are not detectable by chemical analytical methods. Whether these reactions all proceed to the same end-product, for example carbohydrate, we frankly do not know. It is perfectly conceivable that the photosynthetic process consists of serial reactions, proceeding simultaneously, producing products of widely different nature. Each product could result in a different photosynthetic quotient: for example, a product of the empirical composition of a fat with a quotient of less than one, a carbohydrate with a quotient of one, and a hydroxy acid with a quotient of more than one. The total gross reaction might still yield a photosynthetic quotient of one.

How much of the carbon dioxide which is utilized in photosynthesis actually appears as carbohydrate has not been determined with the desired degree of accuracy. But it has never been possible to account for all of the carbon dioxide reduced as carbohydrate. It is true that taking the plant as a whole it is primarily composed of carbohydrate material of one kind or another and of close relatives of carbohydrates such as the uronides. Yet it must be borne in mind that the majority of this constitutes structural material, such as cellulose.

It may well be asked why it is of such importance to know whether a carbohydrate is the first and only product of photosynthesis. Is this simply an interesting academic problem or has it broader significance chemically and biologically?

If carbohydrate is the only substance formed in the photosynthetic process then it follows that the vast array of compounds found in plants must arise from this mother substance by various biosynthetic reactions. It need hardly be pointed out that among these are a great many substances of economic importance such as rubber, fats, waxes, and many drugs. On the basis of this state of affairs carbohydrates assume an enormously important role in the economy of nature, and sugar may in fact be considered the beginning of all organic chemistry. Whether this mother substance is glucose, sucrose, or starch, as has been so much disputed, would be of no immediate significance.

If, on the other hand, carbohydrate is not the only product of photosynthesis, even though the other products are formed in relatively small amounts as compared to the sugar, our reasoning on the mechanism of the photosynthetic process and of the subsequent steps followed in the plant would be materially modified.

We cannot now enter upon a full discussion of this point, but its significance may be briefly indicated. It is well known that plants vary greatly in the relative amounts of different kinds of organic material which they contain. For example, while many plants contain relatively large amounts of carbohydrate material and little hydrocarbon, others, such as certain marine diatoms, contain an astonishing amount of hydrocarbon and little carbohydrate. We are completely in the dark as to how these hydrocarbons are formed, or to what cause this difference in composition may be ascribed. But certain questions immediately present themselves. Are these hydrocarbons the direct result of photosynthesis or do they arise through metabolic changes from carbohydrate material? Is it possible that in different environmental conditions plants may be induced to produce a relatively larger proportion of one or another of these substances? Could it then be possible that under other environmental conditions, such, for example, as existed in early geological eras, plants photosynthesized a higher proportion of hydrocarbons, or that the species or races of plants then covering the surface of the earth possessed this property?

We cannot as yet supply the answers to these questions without entering the realm of speculation. But it is possible to outline some of the experimental avenues of approach which are being followed to gain more exact information on the basis of which we may expect the answers. The methods which are being followed are in part chemical and in part biological, because in so complex a problem it is only through the coöperation of different disciplines that progress can be hoped for.

It is essential to realize that our knowledge of the composition of plants is as yet most fragmentary. Most of this knowledge is confined to cultivated plants. Of the hundreds of thousands of species of plants known only a small fraction has been brought into cultivation and been given any study at all. And most of these were brought into cultivation by primitive man because they met some particular need for food or the arts. But anything like a comprehensive investigation of the nature of the carbohydrates of plants has never been even approached. Add to this the fact that the exact analysis of the mixtures of substances obtained from plants is associated with great difficulties. The compounds which are present in relatively small amounts or which are particularly labile are apt to escape detection. We have described only those

compounds which are easy to isolate. Consequently our generalizations on the nature of the carbohydrates of plants must of necessity be of limited value.

As a first means of approach to this problem there is, therefore, still a good deal to be expected from the results of chemical analysis, and from the improvement of methods of analysis. Emil Fischer made extensive, though futile, efforts to find sugars of the levo series in plants. Yet we now know that at least one levo hexose, *l*-galactose, does exist in plants and has become an easily accessible compound. Other odd sugars, as *d*-manno keto heptose, from the avocado, and pseudo-fructose, reported as a constituent of cane molasses, may be cited as examples that occasionally the search is rewarded with important finds. There is no denying that it may be a long and arduous search, but considering the still untapped possibilities in plant material we must realize that we are only at the beginning.

As everyone who has worked with carbohydrates knows, the available methods for the separation of individual sugars from mixtures are not very satisfactory if only small quantities are present of the substance it is desired to separate. The chemical and physical properties of the various isomers are so very much alike that the methods for their separation depend essentially upon differences in solubilities or boiling points of the carbohydrates or of their derivatives. A similar situation existed in the important group of plant pigments, the carotenoids. Only a few years ago it was thought that there was one carotene and one xanthophyll. By separation through chromatographic adsorption[2] carotene has been resolved into four and xanthophyll into at least twelve different compounds. By converting the sugars into the azobenzene-*p*-benzoyl esters, which are highly colored, the technic of separation by chromatographic adsorption has been applied to glucose and fructose. It may be expected that this general method may be developed into one of great usefulness for analytical purposes.

One result of the search which has been made thus far for different sugars in plants deserves special emphasis. Of the monosaccharides, *d*-glucose appears to be universally present in all plant cells. The plant appears to be geared primarily to the use of glucose for its respiratory processes. Of almost equal universality is *d*-fructose. But these are the only hexoses which have been found in the free state. The plant very readily converts either one of these sugars into the other. Moreover, other hexoses, as mannose and galactose, are readily converted into glucose and fructose within the plant cell.

Besides glucose and fructose plants usually contain sucrose. This is readily synthesized not only from glucose or fructose but also when mannose or galactose are made available to the plant. It may well be that, because of this tendency of plants to convert all simple sugars primarily into glucose, fructose, and sucrose, other monosaccharides, even if they were formed, could not accumulate in sufficient amount in the plant cells to permit detection.

On the other hand, it is in the form of oligosaccharides, glucosides, and polysaccharides that the plant kingdom presents a remarkable variety. These are composed not only of *d*-glucose and *d*-fructose, but include pentoses, methyl pentoses, *d*-galactose, *l*-galactose, *d*-mannose, *d*-sorbose, and heptoses. Many combinations of these, and also these units with the uronic acids, go to make up the tremendously complex compounds which we find primarily in the structural and reserve food tissue. In other words, it may be said that all plants have a common currency which they use for their ordinary running expenses. This is *d*-glucose and *d*-fructose. On the other hand, different species of plants show a very great diversity in the type of investments into which they put their surplus as structural and reserve material. These are the manifold forms of polysaccharides and other sugar condensation products. The latter may be liquidated again into the common currency by means of enzymes which are highly specific and which, in a measure at least, characterize the specific plant groups.

The question may well be asked, therefore, whether all of the monosaccharide units which occur in oligosaccharides, glucosides, saponins, and polysaccharides are produced in photosynthesis. If such is the case, they must be very rapidly converted into the respective condensation products or into glucose and fructose, for most of them do not occur in the plant in the free monosaccharide form. There is a possibility, however, that they are not produced in photosynthesis but rather that the plant has the capacity of effecting changes of the hydrogen and hydroxyl groups in the monosaccharide units of the polysaccharides themselves. This would constitute an intramolecular rearrangement for which we have no sound chemical analog, and it is admittedly difficult to conceive. Yet there is some evidence that such reactions may occur. For example, when leaves containing starch are subjected to desiccation the starch disappears rapidly and the sucrose content increases decidedly. The quantitative relations of the hexoses and sucrose are such that there seems to be no other conclusion but that the sucrose arises directly from starch. There is obviously no satisfactory chemical explanation for this fact, but this much is certain—that the formation and dissolution of starch in the cell is not a simple matter of sugar-starch equilibrium depending upon the concentration of the soluble sugars. The degree of saturation of the protoplasmic colloids seems definitely to control enzymatic reactions, for a reversal of the starch dissolution just mentioned can be attained by increasing the water content of leaves, resulting in the formation of starch. One further point deserves mention in this connection. The immediate products of hydrolysis of starch and of sucrose give quite different results in the plant cell than do ordinary stable glucose and fructose. This is ap-

[2] *Editor's note:* Concerning adsorption analysis, see CASSIDY, "Adsorption analysis: Tswett's chromatographic method," J. CHEM. EDUC., **16**, 88–93 (1939), and RIEMAN, "The quantitative separation of some dyestuffs. An application of the chromatographic method," *ibid.*, **18**, 131–3 (1941).

parently true of respiratory processes as well as of certain metabolic ones. Sucrose greatly exceeds glucose or fructose in its capacity to produce starch when artificially fed to leaves. Whether this is related to the formation of gamma-hexoses or to phosphorylation has proved to be a problem beyond our powers of analysis.

It would appear that for the present at least we are at the limits of utility of our existing methods of chemical analysis. Moreover, the fact cannot be overemphasized that in the carbohydrate economy of the plant, monosaccharides, disaccharides, polysaccharides, and other condensation products are in a constant state of flux. It is only natural therefore that other methods must be tried. Of these a few may be of special interest.

The capacity of plants to accomplish the photosynthesis of carbohydrates is dependent upon the presence of chlorophyll in the leaves. Many plants produce a small proportion of seeds from which chlorophyll-free, or albino plants arise. These seedlings, of course, soon die of starvation because they are not able to manufacture by means of photosynthesis the food material which is needed for their development. They differ from their chlorophyll-bearing brothers primarily in their inability to produce the products of photosynthesis. Such albino plants can, however, be kept alive by artificial nutrition. They provide a means of answering some of the questions which have just been asked. If a single sugar is the only product of photosynthesis, and the plant derives all of its material for growth and the production of the manifold substances normally found in it from this single sugar, it should be possible to produce such a normal plant by artificial nutrition with this sugar. If, on the other hand, other substances are also produced in photosynthesis, which are essential to the normal development of the plant, it may be possible to determine this fact by a laborious process of trial and error. For this purpose albino maize plants have been found to be very satisfactory. Though there still remain many details of technic to be perfected before the main questions can be answered, it has been demonstrated that albino corn plants can be grown for months by artificial nutrition. In a season of four months they produced the same number of leaves as normal plants growing in the field, though the size of the artificially nourished plants was considerably less than that of normal ones. Nor have the albino plants yet been brought to full sexual development and the production of seed. Although the method is only in its beginnings, it has already been demonstrated that the life of the plants can be maintained and new tissue can be formed on an exclusive diet of sucrose. Thus far this has proved to be the best organic nutrient. The testing of the assumptions as to whether sucrose can serve as a mother substance for the production of specific compounds is still in progress.

Needless to say, chemical analysis still plays an important role in this method, yet there are certain advantages in that it combines biological criteria with chemical procedure. The method is applicable to the study of the origin of a wide variety of substances produced by the plant. These include not only the constituents of carbohydrate nature, but also proteins, fats, some drugs, and the important vitamins and hormones which are synthesized by the plant.

As has already been repeatedly pointed out the greatest difficulty in following the course of formation and transformation of carbohydrates in the plant is the maze of reactions which these substances undergo in the living cell. This fact illustrates clearly that the general concepts of the chemist are far too static for the requirements of the biochemist. Even within the single group of carbohydrates the materials involved are in a constant state of flux and change. It has, therefore, long been realized that it would be highly desirable if some of the molecules could be "labeled" or "tagged" so that the course of their alterations could be more definitely followed. Such a means has now been attained through the use of radioactive carbon.

In principle, if we start with carbon dioxide which is radioactive and is thus labeled, we can follow its course, through the various combinations and transformations it undergoes, to its reduction and final elaboration into complex organic compounds. There have been produced two isotopes of carbon, C^{11} and C^{14}, which are being used in experiments of this nature. The C^{11} has a very short half-life period, 20.35 minutes, so that it can be used for only very short experiments, and is not suitable for elaborate chemical investigation of the products formed in photosynthesis. The other isotope, C^{14}, has a very much longer half-life and is more suitable for this type of work. By use of the C^{11} it has been demonstrated that as the carbon dioxide is taken up by the leaf it enters a kind of reservoir which may supply the photosynthetic centers with the raw material for synthesis. Moreover, it has also been possible to demonstrate that the carbon dioxide may, in a measure at least, undergo reduction in the dark. This dark reduction, or incorporation of carbon dioxide into pre-existing organic compounds, is apparently a property of many living things. By the use of radioactive carbon dioxide it has been found to take place in bacteria and in some higher animals as well as in plants.

The elucidation of the further steps in the elaboration of organic material by the plant will require analytical methods of a much higher order of precision than have as yet been applied to this problem. Many of the methods required are still to be developed. The course of the chemical reactions is moreover determined to a large degree by conditions within the protoplast, by enzymes, and possibly by other influences, about which we still know very little. It is to be expected, however, that much useful information on the mechanism of the chemical reactions involved may be obtained from measurements of photosynthesis which are made in conjunction with refined chemical analyses so as to follow through the fate of the carbon dioxide which is absorbed by the plant.

Acids and Bases: Their Relationship to Oxidizing and Reducing Agents

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INTRODUCTION

THE close relationship between oxidation-reduction and acid-base reactions has become increasingly apparent during recent years. A clear understanding of the nature of this relationship was impossible, however, until an adequate theory of acids and bases had been developed. Both the Brønsted and the solvent-system theories were too limited to be of much value in the solution of the problem.

With the advent of the electronic theory of acids and bases (*3*, *4*) the answer has become evident. This paper is a more complete exposition of the ideas suggested in a previous article (*4*). Before considering the relationship between acid-base and oxidation-reduction reactions, a résumé of the fundamentals of the electronic theory of acids and bases is necessary.

THE ELECTRONIC THEORY OF ACIDS AND BASES

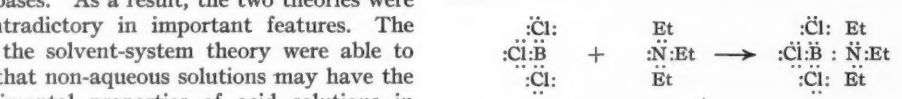
Neither the Brønsted theory nor the theory of solvent-systems explained all the experimental behavior of acids and bases. As a result, the two theories were mutually contradictory in important features. The adherents of the solvent-system theory were able to demonstrate that non-aqueous solutions may have the typical experimental properties of acid solutions in water without hydrogen being present (*4*). In spite of the experimental evidence, the followers of Brønsted maintained that in order to be an acid, a substance must contain hydrogen. Some of them even went so far as to refer to certain substances as "acid-analogous" (*5*, *6*) in order to avoid giving them the name demanded by their properties.

This remarkable insistence upon the presence of some particular element as the "acidifying principle" dates back to Lavoisier's departure from the experimental definitions. Lavoisier tried to make oxygen the necessary constituent of all acids. Davy is rightly credited with the overthrow of oxygen, but should not be blamed for the crowning of hydrogen as the acidifying principle. Davy wrote in 1814, "acidity does not depend upon any particular elementary substance, but upon peculiar arrangement of various substances" (*1*). Davy thus anticipated the view of the electronic theory by more than a century. The reign of hydrogen as the acidifying principle has remained unquestioned until recently. Allegiance is still given it by many chemists, but the revolution initiated by G. N. Lewis in 1923 (*2*) is now well under way.

According to the electronic theory of acids and bases, there is no elementary acidifying principle. The difference between acidity and basicity is one of electron structure. This statement corresponds to the present conception of oxidizing and reducing power. The idea that there is any particular element involved in oxidation is no longer held. A brief statement of the electronic theory of acids and bases follows.

Lewis, for the first time since Lavoisier departed from it, returned to the experimental approach in defining acids and bases. Acids are substances which, like hydrochloric acid, neutralize sodium hydroxide or any other base. Bases are substances which, like sodium hydroxide, neutralize hydrochloric acid or any other acid. Examination of their properties in the light of these definitions shows that acids and bases are identical with Sidgwick's electron-pair acceptors and donors (*7*). *A base can donate an electron pair to an acid to form a coördinate bond. An acid can accept an electron pair from a base in the formation of a coördinate bond. Neutralization is the formation of the coördinate bond between the acid and base.*

A simple illustration of these definitions is given by the reaction between boron trichloride and triethylamine:



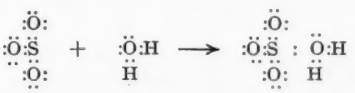
The acidic boron chloride accepts an electron pair from the basic triethylamine. The formation of the bond is neutralization. Consideration of the list of reactions in Table 1 will show that the electronic theory of acids and bases includes both the Brønsted and the solvent-system theories. In the first reaction, the water is a base because it donates an electron pair to the proton from the hydrogen chloride, forming a hydrogen bond.

TABLE 1
ACID-BASE REACTIONS

No.	*Acid*	*Base*	*Neutralization Product*
1	HCl	H_2O	$H_3O^+ + Cl^-$
2	H_2O	NH_3	$NH_4^+ + OH^-$
3	SO_3	H_2O	H_2SO_4
4	H_2O	C_5H_5N	$C_5H_5NH^+ + OH^-$
5	HCl	NH_3	$NH_4^+ + Cl^-$
6	H_3O^+	OH^-	$2H_2O$
7	$SnCl_4$	$2Cl^-$	$SnCl_6^{--}$
8	Cu^{++}	$4NH_3$	$Cu(NH_3)_4^{++}$
9	Hg^{++}	$4I^-$	HgI_4^{--}
10	$Al(OH)_3$	OH^-	$Al(OH)_4^-$
11	$Zn(OH)_2$	$2OH^-$	$Zn(OH)_4^{--}$
12	$AlCl_3$	$COCl_2$	$COCl^+ + AlCl_4^-$
13	BCl_3	C_5H_5N	$C_5H_5NBCl_3$
14	$SnCl_4$	$2SeOCl_2$	$2SeOCl^+ + SnCl_6^{--}$
15	$SeOCl_2$	C_5H_5N	$C_5H_5NSeOCl^+ + Cl^-$

The resulting electrical stress is sufficiently great that in dilute aqueous solution the combination breaks up almost completely into hydronium and chloride ions. In the second reaction the ammonia donates an electron pair to one of the protons in the water molecule.

The nature of the reactants is such that ionization occurs to a much less extent than in the first case. In the third reaction conditions are such that if the acid and base react mol for mol no ions are formed:



In the other reactions whether or not ionization takes place may depend both upon the strengths of the acids and bases involved and upon the dielectric constant of the solvent medium. In any case, the essential feature of the reaction is the acceptance by the acid of a share in a lone electron pair possessed by the base. For other examples and further details the previous paper may be consulted (*4*).

The difference between acids and bases is due not to the presence of a particular element in the acid, but to a complementary difference in their electron structures. Likewise, the difference between oxidizing agents and reducing agents is due not to the presence of a particular element in the oxidizing agent, but to a difference in their attraction for electrons.

ELECTROPHILIC AND ELECTRODOTIC REAGENTS

The experimental relationship between acids and oxidizing agents is a close one. In fact, as has been pointed out previously (*4*), the "typical" effect of an acid solution on metals is due to the oxidizing action of the solvent cation. Usanovich (*8*) attempted to explain the relationship by including oxidation as a special case of acidic behavior. Reduction was considered a special case of basic behavior. Chlorine was listed as an acid and sodium as a base. This has more experimental justification than would appear at first glance. Sodium, when reacting with water, increases the concentration of solvent anions as do bases when dissolved in many amphoteric solvents (*4*). The corresponding property of acids in amphoteric solvents, namely, the increase in solvent cation concentration, is exhibited by chlorine. On the other hand, some oxidizing and reducing agents do not have such properties of acids and bases. For example, the permanganate ion is a strong oxidizing agent, but it is not an acid. It seems, therefore, that a more general classification is necessary—one which will *include* both types of behavior.

Such a classification can be made by dividing the reagents which take part in acid-base and oxidation-reduction reactions into two types. Electrophilic reagents are those which tend to gain electrons in the reactions considered. Electrodotic reagents are those which tend to lose electrons (*4*). (The word electrodotic is coined from the Greek *Didomi*, to give. It was changed from electrodomic at the suggestion of Professor N. F. Hall.) Some reagents may be electrophilic under one set of conditions while under another set of conditions the same reagents may be electrodotic. When a reagent is acting as an acid or an oxidizing agent, it appears to be electrophilic. When it is acting as a base or a reducing agent, it is electrodotic.

Both acids and oxidizing agents are electron acceptors. An acid accepts a share in an electron pair held by a base, while an oxidizing agent takes over completely the electrons donated by a reducing agent. Both are electrophilic and in many cases may act either as acids or oxidizing agents. Both bases and reducing agents are electron donors. A base donates a share in an electron pair to an acid, while a reducing agent loses electrons completely to an oxidizing agent. Both are electrodotic and in many cases may act either as bases or reducing agents.

It is an experimental fact that the same substance may under properly chosen conditions act as an acid, a base, an oxidizing agent, or a reducing agent. For example, water acts as an acid toward ammonia, as a base toward hydrogen chloride, as an oxidizing agent toward active metals, and as a reducing agent toward fluorine. Water is not only amphoteric but is both an oxidizing agent and a reducing agent. This is true of many other substances besides water. Most reagents cannot be arbitrarily classified as acid or base, oxidizing or reducing agent. Their behavior depends upon the specific circumstances of a particular reaction. Therefore, the words electrophilic and electrodotic are relative terms, depending upon conditions. They refer to the behavior of a substance as it acts in the particular reaction under consideration.

A few reagents are listed in Table 2 according to some manifestations of their electrophilic and electrodotic tendencies. The most active oxidizing agent, fluorine, is placed at the top of the list of electrophilic reagents and one of the strongest acids, sulfur trioxide, is at the bottom. The order is roughly that of increasing acid strength downward. The list of electrodotic reagents is arranged correspondingly, with the strongest reducing agent, cesium, at the top and the strongest bases toward the bottom. Apparently some of the strongest oxidizing agents do not act as acids, nor do some of the strongest acids act as oxidizing agents. A similar relationship appears to hold for electrodotic

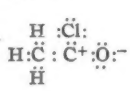
TABLE 2

ELECTROPHILIC AND ELECTRODOTIC REAGENTS

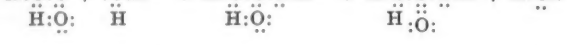
Electrophilic Reagents: Acids and Oxidizing Agents			*Electrodotic Reagents: Bases and Reducing Agents*		
	Number of electrons accepted			*Number of electrons donated*	
Reagent	*Shared, acting as an acid*	*Completely, acting as an oxidizing agent*	*Reagent*	*Shared, acting as a base*	*Completely, acting as a reducing agent*
F_2		2	Cs		1
MnO_4^-		5	Sn^{++}		2
Cl_2		2	I^-	2	1
H_2O	2	2	$(C_2H_5)_2O$	2	?
Fe^{+3}	6, 8, 10	1, 3	C_5H_5N	2	?
Ag^+	4	1	H_2O	2	2
Cu^{++}	8	1, 2	S^{--}	2, 4, 6, 8	2
H_3O^+	2	1	NH_3	2	3
CH_3COCl	2	?	CN^-	2	1
HCl	2		NH_2^-	2	1
BF_3	2		OH^-	2, 4	1
SO_3	2		$(C_2H_5)_3N$	2	?

reagents. Water is listed in both columns because it may behave in any of the four ways depending upon conditions.

Discussion of a few examples from Table 2 should make the others clear. Hydronium ion acts as an acid in accepting an electron pair from hydroxyl ion to form water, but it acts as an oxidizing agent when it reacts with a metal such as zinc to form hydrogen. Silver ion acts as an acid in accepting a pair of electrons from hydroxyl ion to form AgOH. It also acts as an acid in reacting with ammonia or cyanide ion to form $Ag(NH_3)_2^+$ or $Ag(CN)_2^-$. Silver ion acts as an oxidizing agent when it is reduced to free silver. Copper ion reacts in a similar way. Acetyl chloride acts primarily as an acid as do hydrogen chloride gas, boron fluoride, and sulfur trioxide. Acetyl chloride reacts with water in a typically acid fashion. The reaction may be considered as involving the semi-ionic resonance form of the acetyl chloride molecule:



The carbonyl group accepts an electron pair from the oxygen of water:



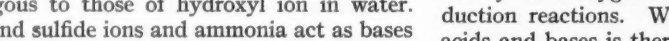
The action of acetyl chloride as an oxidizing agent is more complex and will not be considered here.

In the other column of Table 2, hydroxyl ion acts as a base in sharing a pair of electrons with hydronium ion to form water, but it acts as a reducing agent in giving up electrons to fluorine:

$$2F_2 + 4OH^- \longrightarrow 4F^- + O_2 + 2H_2O$$

The properties of the amide ion in liquid ammonia are largely analogous to those of hydroxyl ion in water. The cyanide and sulfide ions and ammonia act as bases in their reactions with water and in the formation of complex ions with acidic cations. Their reducing power is well known. For example, sulfide ion is readily oxidized to sulfur. Iodide ion is a very weak base, but does react with a strong enough acid, for example, in the formation of the complex HgI_4^{--}. It is, however, a good reducing agent, being easily oxidized to free iodine. Pyridine and ether are weak bases, but their reducing action is rather complex so far as products are concerned. The bonds formed with strong acids are of the typically basic ammonium and oxonium type.

The situation with regard to chlorine is interesting. Chlorine might be called an acid because of its reaction with water by which the concentration of solvent cations is increased:



Obviously, there is some difficulty in deciding whether this is oxidation or an acid-base reaction. Perhaps this example is one indication that even the electronic theory of acids and bases is not yet general enough.

Acids and oxidizing agents are electrophilic. Electrophilic reagents accept electrons from electrodotic reagents in chemical reactions. The electrodotic reagents are bases and reducing agents. If the reaction between electrophilic and electrodotic reagents involves the complete transfer of electrons it is an oxidation-reduction reaction. If it involves the sharing of electrons which the electrodotic reagent donates to the electrophilic reagent, it is the reaction between a base and an acid, *i. e.*, neutralization.

CONCLUSION

Acidity and oxidizing power are merely different manifestations of the electrophilic tendency of atoms, molecules, or ions. Basicity and reducing power are correspondingly different manifestations of the electrodotic tendency of atoms, molecules, or ions. These terms are entirely relative. They depend upon the particular reaction under consideration. Some substances may behave in any one of the four ways depending upon the other substance in the reaction. Even as strong an acid as hydrogen chloride will behave as a base in the presence of a stronger acid such as sulfur trioxide.

The realization that there is no elementary "acidifying principle" is as important to a systematic understanding of chemistry as was the corresponding discovery that oxygen is not necessary in oxidation-reduction reactions. When the fundamental nature of acids and bases is thereby better understood, the relationship between acidity and basicity and oxidizing and reducing power becomes apparent.

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AS WE go to press, we have just received word of the sudden death of Dr. Frederick H. Getman. He will be remembered by readers of the JOURNAL as a frequent contributor, especially to the field of the history of chemistry. We join with his many friends in the Division in paying our respects to a distinguished chemist and an excellent friend.

Monomolecular Film Demonstrations

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IN RECENT years the concept of monomolecular films and layers has entered largely into the explanation of such diverse phenomena as lubrication, contact catalysis, emulsification, and the subject of adsorption in general. In view of the importance of such films, simple and reasonably accurate lecture demonstrations are needed to illustrate the principles involved. In this paper two such methods are given.

Monomolecular films which lend themselves most readily to study are those of the fatty acids and alcohols on a water surface. Rayleigh (*1*) first suggested that such films were unimolecular, and Langmuir (*2*) pointed out that the molecules must be oriented vertically with the polar carboxyl and hydroxyl groups in the water. A measurement of the film thickness then gives the value for the length of the molecule. Most of these studies have been conducted with a surface-pressure balance. This instrument gives accurate results for the length and cross-sectional area of the molecules of the film, but for lecture table demonstration, simpler methods which do not sacrifice too much accuracy are more suitable.

The methods described in this paper give results which compare favorably with those obtained by the use of the surface-pressure balance, yet require no special apparatus. By these methods the physical dimensions of the molecules of the film can be determined in about five minutes.

METHOD I

This method is a modification of that described by Holmes (*3*). Instead of blowing the film into one end of the container to measure its area, a technic which offers considerable difficulty, the entire surface is covered with the film, and the measurement of its area is thus simplified. That this would be a convenient method for the determination of film area was suggested to the author by an account of Langmuir's talking motion picture "Experiments with Oil on Water" (*4*).

Apparatus.—A white enameled dish of the type used by photographers (20 × 31 cm. in size) serves the purpose of this experiment very well. The inside of the dish is paraffined completely, care being taken to cover the edges of the dish. This is conveniently done by applying a solution of paraffin in benzene with absorbent cotton.

The fatty acid or alcohol used to form the film is dissolved in pure benzene, a convenient concentration being 0.2 to 0.3 mg. per ml. For applying this solution to a water surface, a dropping pipet is used. In order to deliver small drops, the tip of the pipet is drawn out to a bore of about one mm. The number of drops of the solution per ml., delivered by the pipet, is measured for each film-forming substance used.

Procedure.—The paraffined dish is filled nearly to the brim with distilled water. A clean water surface, *i. e.*, one free of oily film, is achieved by dusting precipitated manganese dioxide from a cloth bag on one corner of the water surface. The floating manganese dioxide, together with any contamination on the surface, is then blown to the opposite corner and, by tilting the dish, over the edge into the sink. This operation is repeated until the manganese dioxide, after being blown across the water surface, occupies an area of only a few square centimeters. Manganese dioxide was chosen for this purpose because it shows up well against the white background of the dish.

A number of drops of the benzene solution of the substance being used to form the film are placed on the water surface. The drops spread immediately, and the benzene evaporates. The surface is dusted lightly with manganese dioxide, and by blowing gently into one corner of the dish, the film is pushed across the surface into the other end of the dish. The addition of drops of solution to the surface is continued until the film can no longer be blown out of a corner of the dish. The monomolecular film then completely covers the water surface and its area can be easily measured. Whether or not enough drops have been added can be checked at this point by adding one more drop of solution. If the surface is completely covered, the drop does not spread, but floats as a lens-shaped globule. Both Langmuir (*4*) and Blodgett (*5*) have shown that a drop of polar oil does not spread when the surface is completely covered by a monomolecular film.

The data for a typical experiment with palmitic acid follow.

Calculation of Molecular Length

Concentration of solution = 0.000281 g. per ml.
Dropping pipet delivered 72 drops per ml.
Number of drops required to cover the surface = 27
Density of palmitic acid = 0.857

$$\text{Weight of acid in the film} = \frac{27}{72} \times 0.000281 = 1.05 \times 10^{-4}\ \text{g.}$$

$$\text{Volume of acid} = \frac{1.05 \times 10^{-4}}{0.857} = 1.23 \times 10^{-4}\ \text{cc.}$$

Measured area of the film = 530 $cm.^2$

$$\text{Thickness of film} = \text{length of the molecule} = \frac{1.23 \times 10^{-4}}{530} = 23.2 \times 10^{-8}\ \text{cm.}$$

Calculation of Cross-Sectional Area per Molecule

Weight of palmitic acid = 1.05×10^{-4} g.
Molecular weight = 256

$$\text{Number of molecules in the film} = \frac{1.05 \times 10^{-4}}{256} \times 6.06 \times 10^{23} = 2.50 \times 10^{17}$$

Area of the film = 530 $cm.^2$

$$\text{Area per molecule} = \frac{530}{2.50 \times 10^{17}} = 21.2 \times 10^{-16}\ cm.^2$$

TABLE 1

Substance	Number of Carbon Atoms	Method I: Length of Molecule in Cm. $\times 10^{-8}$	Method I: Area in Cm.^{2} $\times 10^{-16}$	Method II: Length of Molecule in Cm. $\times 10^{-8}$	Method II: Area in Cm.^{2} $\times 10^{-16}$	Accepted Value*: Length of Molecule in Cm. $\times 10^{-8}$	Accepted Value*: Area in Cm.^{2} $\times 10^{-16}$
Palmitic acid	16	23.1	21.5	22.5	22.0	24.0	21.0
Cetyl alcohol	16	22.7	21.5	22.0	22.2	22.4†	21.0†
Stearic acid	18	25.7	21.5	24.7	22.4	25.0	22.0
Oleic acid	18	11.2	46.4	13.3	39.2	11.2	46.0
Myricyl alcohol	31	39.4	24.3	39.6	24.4	41.0	27.0

* Values of LANGMUIR, *J. Am. Chem. Soc.*, **39**, 1848 (1917).
† ADAM, *Proc. Roy. Soc.*, **A101**, 452 (1922).

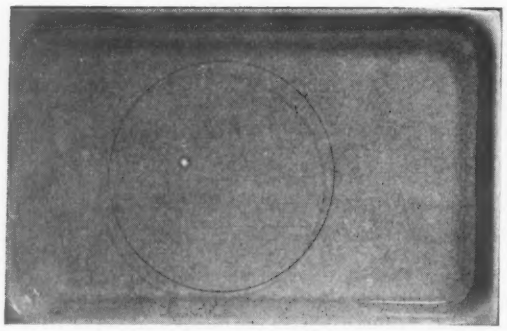
METHOD II

This method is of considerable interest in that it gives visual evidence of the spreading pressure of polar films on water surfaces. The results obtained for the dimensions of the molecule are, however, not as good as those obtained by Method I.

Blodgett (*5*) has described the use of a waxed silk thread to mark the boundary of a monomolecular surface film. In this method this technic is used to measure the film area.

Procedure.—The ends of a piece of waxed nylon thread about one meter in length are tied together to form a loop. This is placed, with the sides of the loop nearly in contact, on a cleaned water surface in a large white enameled tray (42 × 52 cm. in size). If the water surface is clean, the sides of the loop can be brought into contact by gentle blowing. A benzene solution of the film-forming substance is then dropped on the water surface confined by the loop. Immediately the benzene evaporates, and the spreading pressure of the fatty acid or alcohol causes the sides of the loop to be pushed out. Drops of the solution are added to the surface until a drop will no longer spread. When this point has been reached, the loop forms a perfect circle floating on the surface of the water. The diameter of the circle is measured, and the area of the film can be easily computed.

The average results obtained by the two methods for the molecular length and cross-sectional area of a number of substances are shown in Table 1, together with the accepted values for these dimensions.



NYLON THREAD ON A WATER SURFACE, FULLY EXTENDED TO A PERFECT CIRCLE BY AN OLEIC ACID FILM

Within the circle may be seen a lens-shaped globule of a benzene solution of oleic acid which has failed to spread because the area enclosed by the thread is completely covered by the film

DISCUSSION

It is necessary in Method I to paraffin the dish, since otherwise the film will creep over the edge, and its area cannot be accurately determined. This difficulty does not arise in Method II.

Distilled water must always be used, as Blodgett (*5*) has shown that, at a pH of 5 or more, the combination of fatty acids in a monomolecular film with calcium and other divalent ions normally present in tap water results in films with different characteristics.

Whether or not the film-forming substance produces a liquid or solid film is easily determined in Method I. If the film is liquid, "convection currents" are set up by gentle blowing across the surface, as is shown by the movement of the particles of manganese dioxide. Of the substances mentioned in this paper, only myricyl alcohol formed a solid film under the conditions existing in Method I. Langmuir (*2*) has shown that palmitic acid forms a liquid film at low surface pressures, and that the film becomes solid under a pressure of a few dynes per cm. This would indicate that in Method I the films are measured at nearly zero surface pressure and are of the "expanded" type.

In Method II it was found that with a nylon thread there is less leakage of the molecules of the film past the thread than when a silk thread is used. The strands making up the nylon thread tend to lie side by side on the water surface, forming a barrier to the molecules.

These demonstrations have been found to be of value not only in teaching surface chemistry, but also in organic chemistry, since they provide experimental proof that in an homologous series the length of the carbon chain does increase with the number of carbon atoms. The fact that measurements on oleic acid films give a value for the length of the molecule much smaller than the number of carbon atoms would indicate is no doubt due to the presence of the double bond midway along the carbon chain. It is possible that this double bond, as well as the carboxyl group, is anchored to the water surface; *i. e.*, that half the molecule lies along the surface of the water. This would account for the abnormally low molecular length and the high cross-sectional area obtained for the molecule by surface film studies.

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Calculation of the Valence Angle

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IN THE recent paper by Gombert[1] on "The Valence Angle of the Carbon Atom," a rigid geometric proof is given for the correctness of the commonly accepted value for the tetrahedral valence angle. Believing that the pedagogical significance of this demonstration should be emphasized, I am presenting herewith, in amplification, an alternative method of calculation together with some comments on the geometry involved.

The method of approach differs from that used by Gombert in that the geometry of the tetrahedron is here considered in relation to that of a surrounding cube. This way of looking at the tetrahedron in its relation to an enveloping cube facilitates the calculations; it also aids greatly in visualizing certain crystal structures which involve tetrahedral groups of atoms.

Many people find difficulty in grasping the spacial significance of the diamond structure as simultaneously a tetrahedral and a cubic arrangement of the carbon atoms. The unit crystal cell of the diamond is a cube having carbon atoms at its eight corners and in the center of each of its six faces. There are four other carbon atoms within the body of the unit cube. Thus eighteen atoms must be shown in illustration of the unit cell, although statistically there are only eight atoms within the cell boundaries, the corner atoms and the face-centered atoms being shared with neighboring cells.

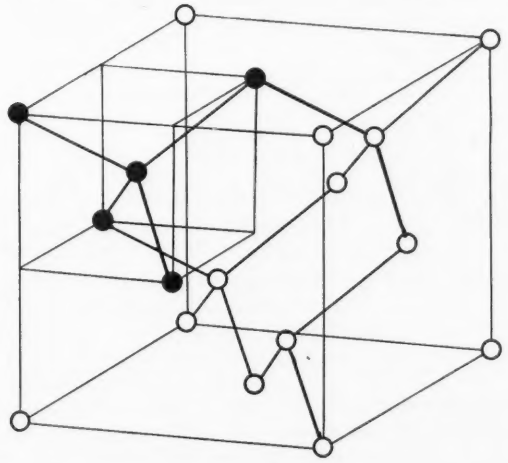

FIGURE 1

Figure 1 represents the cubic unit cell of the diamond crystal with all of the atoms in their correct positions as established by X-ray analysis. In order to emphasize the simultaneous tetrahedral and cubic arrangement of these atoms, a smaller cube is lined in having an edge half as long as the unit cube and having a volume one-eighth as large. The circles representing the carbon atoms in this smaller cube have been blackened. Four of these atoms are on four non-adjacent corners of the cube and there is one in its exact center. When the

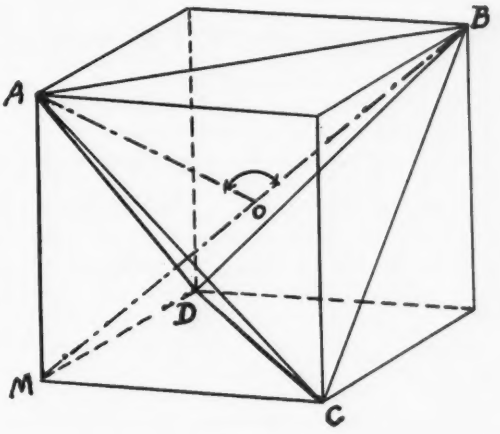

FIGURE 2

corner atoms are joined by diagonals across the faces of the cube it will be seen that the figure so produced is a true tetrahedron bounded by four equilateral triangles (see Figure 2). The central carbon atom is at the center of the tetrahedron as well as of the smaller cube. Thus the lines joining the central carbon atom to the four surrounding carbon atoms (in Figure 1) show the true positions of the valence bonds.

The value for the valence angle AOB (Figure 2) may be readily calculated from the relationship between the tetrahedron and its enveloping cube. If the length of the edge of the cube be designated as E, the face diagonal

$$\overline{AB} = \sqrt{2E^2}$$

Then in triangle ABM,

$$\text{tangent of angle } ABM = \frac{\overline{AM}}{\overline{AB}} = \frac{E}{\sqrt{2E^2}} = \frac{1}{\sqrt{2}} = 0.7071$$

and

$$\begin{aligned} \text{angle } ABM &= 35°15'49'' = \text{angle } BAO \\ \text{angle } AOB &= 180° - 2 \times (35°15'49'') \\ &= 109°28'22'' \end{aligned}$$

A three-dimensional representation of the relation between a tetrahedron and its surrounding cube may be easily constructed from cardboard. An equilateral triangle is cut out and subdivided into four smaller equilateral triangles by cutting with a knife part way through the board. The three corner triangles are

[1] GOMBERT, J. CHEM. EDUC., **18**, 336 (1941).

then folded backward until their edges meet. The edges are then joined together by means of Scotch tape, forming a tetrahedron. If the tetrahedral edge has a length S, the related cube will have a face diagonal equal to S and the length of the cube edge E will be such that

$$S = \sqrt{2E^2}$$

To construct the surrounding cube a strip of cardboard with length four times E and width E is subdivided into four squares by cutting part way through the board, then folded into an open cube and the edges joined. The tetrahedron may then be slipped into the space between the four walls of this open cube. Practical dimensions which give a neat fit are 4.8 cm. for S and 3.5 cm. for E.

A Laboratory Course in the Chemistry of Powder and Explosives

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AS A part of the Engineering Defense Training Program, there has been outlined an intensive eight weeks' course in the chemistry of powder and explosives, the stated purpose of which is "to provide training in the chemistry of explosives for persons planning to work in explosives and loading plants as (1) inspectors for the Ordnance Department and (2) operators for the manufacturers having contracts in this field." The last four weeks, Part B of EDT Outline 11, deal with the classification, chemical properties, manufacture, analysis, testing, and use of explosive materials and their raw material supply.

The following suggested outline of the laboratory portion of this course is the result of the experience of the authors in presenting EDT-9, a twelve weeks' course.

OUTLINE OF COURSE

I. Preliminary Demonstrations and Physical Testing
- A. Safety demonstrations
  1. Safety measures to be followed (*3*)
  2. Firing of blasting caps
  3. Use of goggles, glass screens, etc.
  4. Wearing apparel, "pocket inspection"
- B. Dennis bar test
- C. Primer test
  1. Technic employed in accumulating data
  2. Determination of probability curve
- D. Drop test (*4a*)
  1. Demonstrations on general functioning of explosives
  2. Experiments actually performed by students
- E. Sand bomb test
- F. Pyrotechnics (*4b*)

II. Nitrocellulose
- A. Analysis of raw materials
  1. Cellulose
     (*a*) Moisture
     (*b*) Ash
     (*c*) Alkali-soluble
     (*d*) Lime, chlorides, and sulfates
     (*e*) Hypochlorites
  2. Ethyl alcohol
     (*a*) Specific gravity
     (*b*) Acidity
     (*c*) Residue on evaporation
  3. Ether
     (*a*) Non-volatile residue
     (*b*) Acidity
  4. Analysis of mixed acids
     (*a*) Suspended matter
     (*b*) Ash
     (*c*) Total acidity
     (*d*) Total HNO_3
     (*e*) Oxides of nitrogen
     (*f*) Sulfuric acid and water
     (*g*) Specific gravity
- B. Nitrocellulose
  1. Nitration of cellulose (preserve nitrating mixture for II-A-4)
  2. Testing nitrocellulose
     (*a*) Solubility—gravimetric method
     (*b*) Determination of nitrogen
     (*c*) Ash—HNO_3 digestion

III. Propellants
- A. Smokeless powder
  1. External moisture—water dried
  2. NG and DNT (*1*) and DPA (*2*) determinations
  3. Graphite
  4. Total volatiles
  5. Ash
  6. Dimensions
     (*a*) Length and diameter
     (*b*) Grain and perforation diameter
     (*c*) Web measurements
  7. Demonstration of heat test at 134.5°C.

B. Black powder
   1. Sampling
   2. Moisture
   3. Specific gravity
   4. Granulation
   5. Chemical analysis (KNO_3, S, C)
      Hot aniline method for S(*5*)

IV. High Explosives
   A. Trinitrotoluene
      1. Preparation and purification (*6*)
      2. Analysis of du Pont TNT
         (*a*) Solidification point
         (*b*) Insoluble matter
         (*c*) Moisture
         (*d*) Acidity
         (*e*) Color
         (*f*) Granulation
   B. Amatol
      1. Moisture
      2. Analysis
         (*a*) TNT
         (*b*) NH_4NO_3
   C. Tetryl
      1. Melting point
      2. Acidity
      3. Insolubility in C_6H_6
      4. Moisture
      5. Color
      6. Granulation
      7. Abel test
      8. Microscopic examination of granular and crystalline forms
   D. Lead azide and mercury fulminate
      1. Drop test
      2. Ignition test
      3. Sand bomb test

SAFETY FACTORS

Safety demonstrations have been placed first in the outline because this subject cannot be overemphasized in the training of an explosives inspector or worker. The wearing of goggles must be an inflexible regulation, if the proper attitude is to be developed and if the effects of possible accidents are to be minimized. Safety glass screens are used to shield operators and to isolate individual experiments. These relatively light barricades effectively stop the fragments from the small explosions which might occur. The carrying of matches is prohibited and frequent pocket searches are valuable. Smoking is absolutely prohibited in the laboratory and in or near the magazines.

One person is made entirely responsible for all laboratory operations. No experiment is performed without his approval and no change is made in any procedure unless the supervisor is consulted. This eliminates completely the carrying out of incompatible operations in the same laboratory. Very few laboratories have been designed for exclusive work on explosives and therefore very strict supervision and careful planning must be exercised if difficulties are to be avoided. Centralized authority is the solution of this problem.

Laboratory operations which are the greatest potential hazards to personnel or apparatus are conducted by the demonstration method. This does not actually lessen the exposure but it does minimize the hazard by eliminating poor technic. With proper technic, most of the laboratory work is no more dangerous than the usual experiments in organic chemistry. If the conduct of these more hazardous tests is given the undivided attention of an intelligent instructor, no accidents should occur.

Benzene, toluene, aniline, and their nitro derivatives are extremely poisonous, and should be handled with this in mind. The chief essential in avoiding accidents is to make the inexperienced student fully conscious of every movement in handling explosives, training him "to play safe" until he is automatically careful at all times.

One of the primary problems encountered in setting up a laboratory is that of storing the explosives. Because of the variation in facilities from one school to another, no specific solution can be suggested. In our particular case, magazines were located in a fenced field and a second fence of the "climb proof" type was built around the magazines. The gate on the inner fence and the magazine doors are heavily padlocked. The magazines themselves consist of sections of 4-foot concrete sewer pipe sunk into the ground. The bottoms are sealed and the inside is lined with heavy fiber board. A small wooden superstructure seals the top from rain and permits access to the magazine. All shelves are below the level of the ground so that the explosives are effectively protected from projectiles. Samples of each explosive are stored separately in small boxes to facilitate removal of samples and to prevent tipping of bottles. A magazine containing 10 pounds of explosive should be at least 40 feet from all paths, roads, buildings, etc.

One person with undivided authority is designated to handle and to store all explosives in the magazine. He alone may store or remove material from them. This reduces the possibility of improper storage or the delivery of wrong samples. No container is ever opened in or near the magazine. In this manner, absolute cleanliness is maintained. Boxes of explosives are opened with a hardwood wedge and hardwood mallet, or specially designed non-sparking tools, outside of the magazine and at a distance from it. The use of such tools as steel hammers, hatchets, or chisels is prohibited. Explosives are stored only in the magazines designated for that particular type of material. Primers and primer materials are never stored with high explosives. Black powder must also be kept separate from high explosives. The quantity and type of explosives removed from the magazine for use in the laboratory is that which is estimated to be necessary for a single day's experiments. Any excess is returned daily by the person in charge. Explosives should never be left about the buildings or grounds. Frequent inspections

of the magazines should be made by a responsible person in the company of the man in charge of the magazine.

LABORATORY DETAILS

Having completed certain demonstration phases, the members of the class may be divided into groups and introduced to the various pieces of apparatus used in the physical testing. The equipment for this work is neither elaborate nor expensive and may be readily constructed in a small shop. To simulate the Dennis bar test, one end of a piece of steel ($1/2'' \times 1'' \times 30''$) was fastened to the surface of a hot plate and a temperature gradient was set up. Minute quantities of powders and explosives were placed at various positions and the reactions were observed.

Figure 1 illustrates the type of apparatus used in the primer test and the drop test. For the primer test, the firing-pin spring was removed from a single-shot, bolt-action, .22 caliber rifle. The stock was removed and the barrel and action were mounted vertically. A four-ounce steel ball was dropped from an adjustable electromagnet. The following distances—3, 5, 7, 9, 11, 13, 15 inches—have been found to give satisfactory curves with 100 rounds of .22 caliber blanks fired at each position. The gun mounting may be moved to one side and a steel weight (2 kg.), replacing the steel ball in the primer test, falls on a specially constructed steel surface set on the base (*4a*).

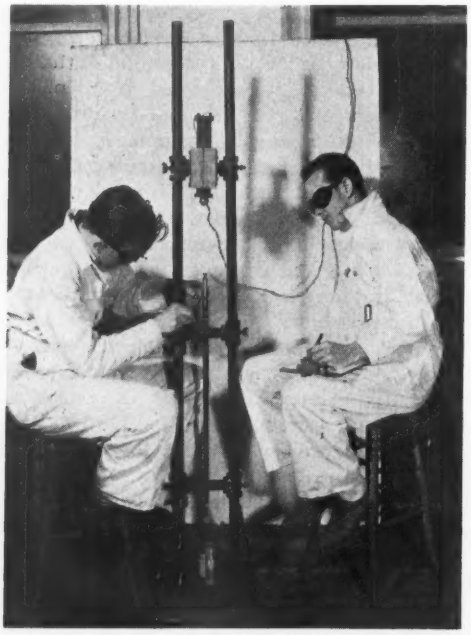

FIGURE 1.—APPARATUS FOR PRIMER AND DROP TEST

A set of No. 6 caps, obtained from the Western Cartridge Company and filled with varying amounts of explosives, was used in the sand bomb test. The functional characteristics of the ingredients present in pyrotechnics may be set up as a demonstration (*4b*). Although these two tests are included in the introductory phase, it is suggested that they be performed toward the end of the course. The student will then be in a position to interpret the data more completely.

The testing and inspecting of raw materials, powders, and high explosives are based on the procedures taken from War Department Technical Manual 9-2900 (*7*). Where this information is incomplete, literature references have been cited. More experiments have been outlined than can be completed in the time available for the advanced course. Many of the items are repetitions, however, so that a number of them can be eliminated. The omission of particular sections may be a matter of opinion but the hazards involved will be found to be an excellent criterion for this selection. Where possible the authors selected experiments involving cellulose in preference to nitrocellulose, and TNT instead of tetryl. Experiments with lead azide and mercury fulminate were demonstrated for the laboratory groups.

No difficulties are experienced in the analysis of the raw materials used in the manufacture of smokeless powder. Certain precautions for the balance of the work are listed below. In the determination of total HNO_3 with the du Pont nitrometer, it is absolutely compulsory that a nitrometer mask be worn. No samples of student-manufactured nitrocellulose should ever be dried, as these may be extremely unstable. The heat test at 134.5°C. on smokeless powder of recent manufacture may be demonstrated only. Extreme caution should be exercised in the analysis of black powder since this material is particularly sensitive to spark, flame, or friction. Students should never be permitted to run tests on their own preparations. Only materials of known stability should be tested. The stability test on nitrocellulose was purposely omitted since elaborate equipment is required.

ACKNOWLEDGMENT

The authors are indebted to the members of the technical staff of the Western Cartridge Company, East Alton, Illinois, for their valuable assistance and advice.

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Problems of Teaching Quantitative Analysis

II. Students' Laboratory Records

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ALL instructors of quantitative chemical analysis, who are themselves experienced analysts, would undoubtedly agree that making actual determinations is of prime importance in training a student in analytical work. Broadly considered, this laboratory work consists of two parts, the performance of the exercises and the preparation of the record of the results obtained. Although the former of these operations is of first importance, the latter comes a close second. Few quantitative determinations are worth making if the data do not merit recording.

Although the preparation of an adequate and reliable record of quantitative data is a fundamental requirement for a satisfactory experimental worker, an examination of the laboratory report books of students coming as graduates or transfers from many institutions has revealed extensive examples of mediocre record making. Two possible conclusions seem inevitable. The students were not informed concerning the desirable characteristics of a well-kept record; or, if so, they were not required to incorporate these points in their own books. It has seemed worth while, therefore, to consider briefly the general problem of handling numerical results obtained in the laboratory. Few texts, either for elementary or advanced quantitative analysis, give more than brief mention of this subject.

NATURE OF ANALYTICAL RECORDS

The kind of notebook employed in different laboratories varies widely. Some use is made of books having the frequently recurring entries printed,[1] with blank spaces for entering the data and the variable items. Much more frequently the book consists entirely of blank pages. Permanently bound books are generally used, but loose, single sheets are preferred by some instructors.

With large classes the use of printed form books is a very efficient practice, particularly for the instructor. The general use of blank books in industrial laboratories, however, led the senior author, after years of experience with the other type, to adopt this form in order to give practice in preparing a satisfactory report under such conditions.

Although conscientious instructors would not care to leave students entirely without advice on submitting records in blank books, neither would these teachers agree on the extent to which persons should be regimented in such matters. Generally the development of individuality is to be encouraged, but modern industrial practice requires both reliability and efficiency. It seems desirable, therefore, to provide approved examples and then to have the student adapt these to the specific determinations assigned.

A book of this kind could include a number of printed records as examples to show the items that should appear and how to arrange them in a reasonably usable form. In view of the content of most elementary courses, these examples might best be confined to the more common kinds of titrimetric and gravimetric measurements. Contrasting kinds of type, if used, would distinguish between what would be printed in a prepared book and what the analyst would insert. After making their own records for a semester of such work, capable students should be able to arrange the requisite data for other kinds of measurements.

Engineering students may be expected to use plain slant or vertical lettering in preparing such records. Others will be amply rewarded for acquiring proficiency in this art.

As with the type of book selected, there is no uniformity in the form followed in recording data in blank books. The arrangement to use and the specific items to include are two points of much importance. In both of these points variation is found with different kinds of methods of measurement. The general requirement of a report considered satisfactory from this viewpoint may be summarized by the statement that another analyst should be able at any time to take the book and determine easily from the record what was done and how the information was obtained. It should be a clear and complete record to any one "skilled in the art."

DATA REQUIRED

To have the book meet this test, in general the record should contain entries covering the following points: (1) date of the determination, including the date of receiving the sample, if this is important; (2) designation of the sample, in the form of a serial number or other distinguishing mark; (3) condition when received, and the source, if significant; (4) name or formula of the constituent determined, or the name of the property measured, including the kind of material examined; (5) method of determination used, with at least one reference to a source containing details[2] of

[1] Examples are: MAHIN, "Analyst's record," Lafayette Printing Co., Lafayette, Ind., 1920, and ENGELDER, "Laboratory record book in quantitative analysis," John Wiley and Sons, Inc., New York City, 1938.

[2] The first reference should be the textbook being followed, the items including author, title, page, and year of publication; *e. g.*, Mellon, "Methods of Quantitative Chemical Analysis," p. 225 (1937).

procedure; (6) amount of sample taken, except in the unusual cases when it does not have to be measured; (7) readings for the measurement of the desired constituent or property; (8) amount of the desired constituent found, expressed in appropriate terms[3]; and (9) the signature or initials of the analyst.

All of this information should be placed on the *right*-hand page of blank books. In addition, on the preceding *left*-hand page, there should appear balanced chemical equations for all the essential reactions concerned in the procedure, together with a sample calculation, preferably with logarithms, to show that the correct method was followed. If desired, brief notes may be added concerning any special items that should come to the attention of the one who is to inspect the book. The accompanying report for soda ash illustrates these points.

RULES

In entering analytical data in the record book, in accordance with the forms proposed, instructors will generally agree that compliance with the following specific rules is desirable:

1. Enter all records in ink. Measurements should be recorded directly in the book as *soon as read*. Do not use loose sheets for recording data of a permanent character.
2. At the time an exercise is begun fill out all headings as far as the experimental work permits.
3. In recording measurements where subtractions are to be made place the smaller value underneath the larger, whether the latter is obtained first or last.
4. Use the proper number of significant figures and include the intended zeros. Thus a volume of 30.00 ml. should not be recorded as 30 ml.

Unless otherwise directed, percentages are to be calculated as far as the third, and rounded off to the second, decimal place. In reporting the average of two or more determinations the result should be to one decimal place if the difference between the extremes is more than 0.1 per cent, and to two decimal places if the difference is 0.1 per cent or less. (In applying this principle of calculating averages to only one uncertain figure, more than two decimal places are necessary in dealing with very small amounts of constituents.)

5. Do not make erasures or detach pages. If a report is ruined or an exercise is to be repeated, draw a line diagonally across the rejected page and begin a new record upon the next blank page.
6. Do not put data for more than one determination upon a page.

INSPECTION AND GRADING

Before submitting for inspection the results of any exercise, the student should examine the record critically. Are all equations for the essential reactions in-

[3] Frequently analysts determine physical properties, such as density, which involve no calculation of the amount of a constituent.

(To be entered on right-hand page)

No. SA 35 3/15/'41

ALKALINITY OF SODA ASH

Titration with HCl, in presence of modified methyl orange

Ref. 1: Mellon, "Meths. Quant. Chem. Anal.," p. 227 (1937).
Ref. 2: Treadwell-Hall, "Analytical Chemistry," II, 510 (1935).

Sample:	I	II
Container + sample	20.3901	20.1341
Container	20.1341	19.8803
Sample*	0.2560	0.2538
Constituent determined:		
HCl Eq. (Na_2CO_3) = 0.005300 g.		
Vol. used, final†‡	40.20	39.80
Vol. used, initial	0.00	0.00
Ml.	40.20	39.80
G. Na_2CO_3 found	0.2131	0.2110
% Na_2CO_3	83.23	83.12
Average %	83.2	
% Na_2O	48.7	
	Signature	

(To be entered on left-hand page)

CHEMICAL REACTION

$$2HCl + Na_2CO_3 \longrightarrow 2NaCl + H_2O + CO_2$$
$$2\,(36.46)\text{ g. HCl} \Rightarrow 106.00\text{ g. } Na_2CO_3$$

SAMPLE CALCULATION

$$1\text{ ml. HCl soln.} \Rightarrow 0.005300\text{ g. } Na_2CO_3$$

$$\%\ Na_2CO_3\S = \frac{\text{Vol.} \times \text{Eq.} \times 100}{\text{Sample}} = \frac{40.20 \times 0.005300 \times 100}{0.2560}$$

log 40.20	=	1.60423
log 0.005300	=	7.72428 − 10
log 100	=	2.00000
		11.32851 − 10
log 0.2560	=	9.40824 − 10
log Percentage	=	1.92027
Percentage	=	83.23

$$\%\ Na_2O = \%\ Na_2CO_3 \times \frac{Na_2O\text{ mol. wt.}}{Na_2CO_3\text{ mol. wt.}}$$

* Alternate entry for single, large sample weighed on counterpoised glasses:
Wt. sample
Vol. to which diluted
Fraction used

† Values calculated from calibration curve.

‡ The temperature of the solution should be recorded if correction is to be made for variation from 20°.

§ Factor-label notation (quantities which cancel out are in parentheses):

$$\%\ Na_2CO_3 = \frac{\text{g. } Na_2CO_3}{100\text{ g. sample}} = \frac{40.20\text{ (ml. HCl soln.)}}{0.2560\text{ (g. sample)}} \times \frac{0.005300\text{ g. } Na_2CO_3}{1\text{ (ml. HCl soln.)}} \times \frac{100\text{ (g. sample)}}{100\text{ g. sample}}$$

or

$$= \frac{40.20\text{ (ml. HCl soln.)}}{0.2560\text{ (g. sample)}} \times \frac{0.005300\text{ (g. } Na_2CO_3)}{1\text{ (ml. HCl soln.)}} \times \frac{100\%\ Na_2CO_3}{100\text{ (g. } Na_2CO_3)} \times \frac{100\text{ (g. sample)}}{1}$$

cluded and balanced? Is the sample calculation adequate and correctly stated? Are all the data included which the approved form requires? Is the information given entered in conformity with the rules? Until these questions can be answered affirmatively, the record book should *not* be presented. In case of uncertainty, the instructor should be consulted.

In the belief that carefully supervised elementary laboratory work should bear 50 per cent of the course grade, the authors feel the necessity of stressing the experimental part of the course. From this point, therefore, the recommendations represent personal preference and practice perhaps more than general agreement.

Subject only to penalty for a late report,[4] the student may analyze a given sample as many times as he wishes. *But once the report is submitted, he is through with that sample* (except in some unusual case).

Upon submission, the laboratory report is examined first of all for conformity to the requirements just outlined. The different kinds of deficiencies, if found, are indicated by means of the following stamps: REACTIONS, CALCULATIONS, SAMPLE NUMBER, DATE, CONSTITUENT DETERMINED, METHOD, INCOMPLETE RECORD, RECALCULATE, RULES (1–6), CONSTANT WEIGHTS, and SIGNATURE. If it is necessary to apply one or more of these stamps, the book is returned for correction, with an occasional resultant late penalty because of the delay. When satisfactory in this respect, it is then considered for the quality of the results obtained. If satisfactory, these are stamped ACCEPTED; if not, the stamp is REPEAT EXPERIMENT.[5] In addition to these reasons for rejecting a report, there remains the possibility that the record may be unsatisfactory as regards legibility and neatness. Reservation is made of the right to insist at any time upon reasonable achievement in these respects. At the end of the course a grade is given on the general appearance of the book, in addition to those for each determination.

In order to emphasize the importance of well-kept laboratory records, a penalty is entered against the laboratory grade for each stamp applied indicating unacceptability. The REPEAT EXPERIMENT stamp entails the heaviest penalty, of course.

In case a determination is rejected, the calculations should be checked by the student, since 10 to 20 per cent of all rejections in the authors' classes are traceable to inaccurate calculations. Unless the recalculated value is acceptable, a new sample should be secured.

[4] A schedule is posted listing the minimum number of laboratory exercises required for a passing grade. Following each entry there are two dates. The first shows when an average student should have the exercise accepted. The second is the date after which the report is considered late. In order to provide incentive for the procrastinator to keep his work moving, a grade penalty is attached to late reports, due allowance being made for unavoidable circumstances.

[5] It should be noted that rejection of a result involves no consideration of why it was wrong. Those in charge of commercial laboratories must be able to rely upon their analysts' reports. It makes no difference to a plant manager, for example, when the wrong car load of material is used or sold, whether the weight of sample or its logarithm was mis-read, or unsuitable conditions were maintained for the desired chemical transformations.

THE VALENCE ANGLE OF THE CARBON ATOM

PHILIP F. WEATHERILL

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RECENTLY Gombert[1] showed a method of calculating this angle, using a solid model of the regular tetrahedron.

Considered as a problem in spherical trigonometry, this calculation is extremely simple. Imagine the carbon atom at the center of a sphere. The valence bonds will intersect the surface of the sphere at four symmetrically placed points, forming four equal spherical triangles, the angles of which are all 120°. We wish to calculate the sides of these triangles, one of which, *ABC*, is shown in Figure 1. To find side *AB*, draw *AD* bisecting angle *A*. We now have the right-angled triangle *ABD* in which we know angle *DBA* (120°) and angle *BAD* (60°). By Napier's Rule ("the sine of the middle part equals the product of the tangents of the adjacent parts"):

$$\begin{aligned} \cos \text{ side } AB &= \cot 120^\circ \times \cot 60^\circ \\ \log \cos AB &= 9.7614394 + 9.7614394 \\ &= 9.5228788 \\ \text{side } AB &= 109^\circ 28' 16'' \end{aligned}$$

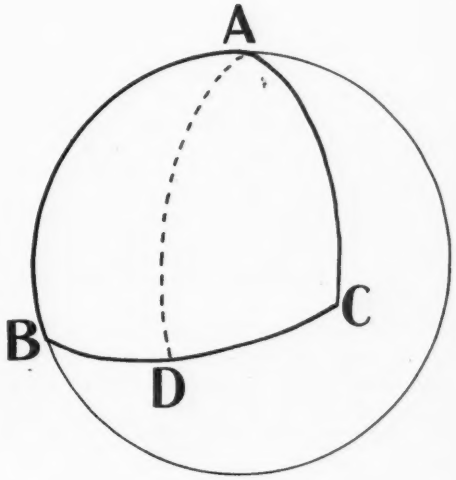


FIGURE 1

[1] J. CHEM. EDUC., 18, 336 (1941).

Portland Cement and the "Plastic" Concrete

R. H. BOGUE[1] *National Bureau of Standards, Washington, D. C.*

OUR interest in things which touch our senses always becomes greater and our pleasure in them is increased as we become more familiar with their history, their origin, and the phenomena surrounding their existence. This is equally true of a flower, a star, a mineral, an insect, or an industrial product. We may drive for a hundred miles out into the country and one man will see only the great variety of flora on the hillsides; another's imagination will be stirred by speculations on the origin of the hills, the canyons, the red clay, and the twisted rock formations along the way; another will find in the products of chemical and engineering skill displayed in the roadbed along which he rides, in the beautiful bridges, in the large buildings, in the homes, and in silos on the farms, that which stirs his keenest curiosity.

The purpose of this writing is to point out among the latter group those structures built of concrete and to dwell briefly on the processes by which they have come into existence in order to arouse in the reader an active interest through a better understanding of them. This will not be the place to go into great detail in descriptions of the chemical or engineering problems which comprise the literature of the cement industry, but rather to give in outline a picture which will arouse conscious pleasure and perhaps the desire to delve deeper into these subjects.

HISTORY OF PORTLAND CEMENT

It is true that concrete is one of the great structural materials of our age. In its modern sense, portland cement concrete is a comparatively new material although its predecessors, in one form or another, date back to antiquity. Among these early structures will be mentioned only the great bridge and aqueduct, once regarded as one of the seven wonders of the world, known as the Pont du Gard, in the old city of Nimes, France. This bridge spans the deep valley of the Gard and is built in three tiers of stone arches, one upon the other, the upper one carrying the so-called *specus* or aqueduct, through which the Romans, twenty centuries ago, supplied the water for their beloved fountains of Nemaunus. This trough, built by Augustus, was lined with a mortar made with cement similar to that used by the Romans in many other great projects, and is today a beautiful example of the durability of that material.

These old structures were usually fabricated with a cement obtained by burning, at a relatively low temperature, some of the impure argillaceous (*e. g.*, clay-containing) limestones of the region, subsequently coarsely pulverized and mixed with a volcanic ash and water.

[1] Director of Research, Portland Cement Association Fellowship.

It was not until 1824 that a bricklayer of Leeds, England, by the name of Joseph Aspdin, applied some of the first principles of experimentation, typical of chemical investigations today. He decided to find out what kind of a cement would result from the use of the hard, sintered clinkers that were accidentally produced in the old vertical furnaces during the burning of argillaceous limes. These clinkers formerly had been thrown out because they were hard to grind, but Aspdin found that the powder produced from them, when mixed with sand and water, gave a structure of enormously increased strength compared with that which had hitherto been known in his industry. Blocks made with this material resembled a natural limestone quarried in Portland, England, used extensively as a building stone. Because of this striking resemblance Aspdin called his newly discovered material "Portland Cement." The stone of Portland is not greatly different in appearance from our own widely used "Indiana Limestone."

But Aspdin went further than this. Having found his chemical curiosity so well rewarded by his first endeavor, he and others of his contemporaries, notably the French engineer Vicat, made extensive studies with various types of lime rock burned at various temperatures and thereby arrived at limiting compositions and burning methods within which the cement produced was of high quality and beyond which the quality became inferior.

These were the beginnings of the portland cement industry as we know it today. Progress at first was not rapid and engineers rather reluctantly adopted the new cement. In the United States in 1880 there were produced 42,000 barrels; in 1900 over 8,000,000 barrels were produced; but by 1928 176,000,000 barrels, of 376 pounds each, came out of the cement plants in the United States. The following years of depression checked the rapid growth of the industry, but by 1940 the production had climbed back to reach 130,000,000 barrels.

MANUFACTURE

We may now ask ourselves, "What is this material, portland cement? From what is it made? Of what is it composed?" Up to the turn of the century there had been accumulated a considerable amount of information on manufacture, but for the most part this consisted of results obtained from studies on heat economy, grinding efficiency, and mill practice. The chemical control might be described as "rule-of-thumb." But from about 1915, new tools of investigation were introduced, research became organized, and the thought of *product quality* became ascendant. The microscopical observations made many years earlier by the great master-chemist of the Sorbonne, Henry Le Chatelier, were at

last applied in the industry and the principles of the phase rule discovered by the American scientist, Willard Gibbs, became basic in cement research. Studies on high-temperature equilibria, thermodynamic balance, and reaction potentials gave increasing understanding to the entire process of cement manufacture. As a result, old operations were revolutionized, ancient vertical stack furnaces gave way to the great rotary kilns of today, and the making of cement began to be a scientifically controlled art. The early rotary kilns were about 60 feet long, but in a few years the demands for greater yields and better heat economy caused the length to be increased and a large number of present-day kilns exceed 300 feet in length and 10 to 12 feet in diameter. In England and Denmark there are two kilns over 500 feet in length. The capacity of a large kiln may be as great as 4000 barrels of clinker (of 376 pounds each) per day.

Simultaneously with changes in plant operation the chemist was attaining a clearer insight into the character of the raw materials, the reactions by which these raw materials are converted at high temperatures to cement clinker, and the reactions by which cement mixed with water and aggregates (that is, sand and crushed stone or gravel) produces concrete. It is through this new knowledge, gained by chemical and physical research, that the portland cement industry has been enabled to meet the challenge of increasing and diversified requirements that is placed upon the structural material, concrete.

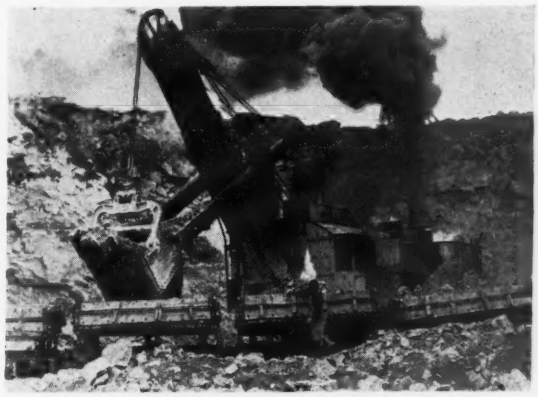
RAW MATERIALS

The raw materials of portland cement must consist of a mixture of minerals which will include a large percentage of lime and a smaller amount of silica. Furthermore, in order that the reactions of cement making may be properly completed, it is important that certain fluxing elements be present and, in the natural economy involved in the selection of such materials, there will always be present variable amounts of alumina, ferric oxide, magnesia, and lesser amounts of other materials. A typical composition after burning off the carbon dioxide, water, and other volatile materials may be about as follows:

	Per cent
CaO	64.6
SiO_2	21.8
Al_2O_3	5.6
Fe_2O_3	3.3
MgO	2.9
SO_3, TiO_2, Na_2O, K_2O	1.6

Any significant departure from a prescribed composition will change the properties of the cement, so that a rigid control of the composition is necessary at all times.

The lime is commonly derived from various types of limestone, chalk, oyster shells, marl, or slag. The constituents of these materials other than lime must, of course, be taken into consideration in proportioning the remaining ingredients of the raw mix in order that the ultimate composition shall be within narrowly prescribed limits. A rock occurring in the Lehigh Valley,



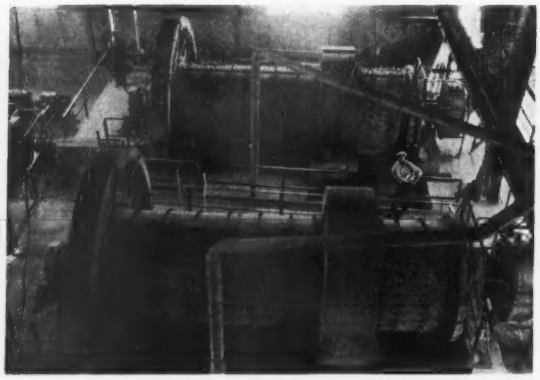
A LIMESTONE QUARRY SHOWING AN AGILE POWER SHOVEL BEGINNING TO LOAD ROCK ONTO CARS

known as Cement Rock, contains these other ingredients in about the correct proportions so that no additional materials are necessary. This, however, is the exception. Usually there must be added some siliceous material which is most commonly clay or shale. Sometimes, however, it is necessary, in order to meet required compositions, to introduce a highly siliceous rock and occasionally some form of iron oxide. In England and some parts of Europe where the lime is obtained from beds of chalk, special devices must be used for taking out the frequently excessive amounts of flint.

The treatment of the raw material prior to burning must be such that a very finely pulverized, intimately disseminated, and uniformly distributed raw mixture results. The nature of this treatment will of course vary with the type of raw material handled. The limestone and clay or shale usually are ground separately during the preliminary stages and mixed for the final grinding, which may be done either in the dry state (known as the dry process) or in a water slurry (known as the wet process). In the early plants the dry process was used almost exclusively but in the past score of years there have been an increasing number of wet process installations. The advocates of the latter process believe that wet mixing results in greater uniformity and that there is less of a dust nuisance. The excess water may be removed by passing through a filter press or, as seems to be preferred practice today, by the use of settling basins.

The composition of a raw mixture containing an excess of certain minerals may be adjusted either by adding a quantity of the deficient mineral or by removing a quantity of the overabundant minerals. For example, a mix containing a deficiency of limestone and an excess of quartz (due to the nature of the available deposits)

may be corrected either by introducing a quantity of high-grade limestone or by removing some of the quartz. The former may involve the expense of transportation of high-grade limestone from a distant source. The



TWO-COMPARTMENT MILLS WHICH ARE USED FOR GRINDING THE RAW MATERIALS THAT LATER ARE BURNED AT VERY HIGH TEMPERATURES FOR THE MAKING OF PORTLAND CEMENT CLINKER

latter may be accomplished by processes of flotation or centrifugation. The principle of flotation, long employed in the mining industry for separating ore from gangue, allows one mineral to be floated from another in a froth produced by the addition of a suitable reagent in a flotation cell. The centrifuge accomplishes the same result through the application of the principle of differences in specific gravity between the minerals it is desired to separate.

Throughout the entire process of producing the raw kiln feed, various means are used for insuring that this feed shall be uniform and of the desired composition. This detail begins in the quarry where samples are taken regularly for analysis and where, by direction of the chemist, the approximately correct proportioning is initiated. Similar analyses are made at every stage of the raw grinding. After the final grinding the slurry, in the case of the wet process, is pumped into a series of tanks and continuously agitated to insure uniformity. The slurry of each tank is separately analyzed and the contents of these tanks may be judiciously combined in a final kiln-feed tank so that minor differences in composition will be eliminated. In the dry process, blending bins and storage bins are used as are the slurry tanks. Here the material is transferred from stage to stage by the use of elevators and conveyors. In all cases the kiln feed is finally analyzed to insure that it is right.

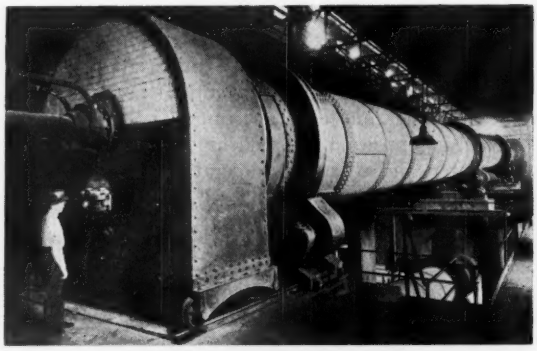
BURNING OPERATION

Up to this point we have been concerned merely with the production of a raw mixture which, when properly burned, will produce cement clinker of the type and having the properties designed. Any deviations from the precision of the proportioning or in the uniformity of grinding will be reflected by variations in the finished product. However, *no* degree of perfection in proportioning or grinding can of itself insure the production of clinker possessing the desired properties. The burning process is crucial. Only by an intensive heat treatment is this raw mixture converted into portland cement clinker. Temperatures of 1450°–1500°C. (2642°–2732°F.) are attained in the hot zone of the kiln, temperatures far above those required to melt steel or glass or aluminum. To withstand such temperatures the huge steel shell is lined with some form of heat-resistant brick.

The raw feed is introduced at the upper end of the kiln, either as a thick slurry or as a dry powder, and the slow rotation of the kiln, which is inclined slightly downward toward the lower end where the fuel is introduced, causes the kiln feed to pass from the upper cool end to the lower hot end. The fuel may be oil, gas, or pulverized coal, blown in under high pressure with the proper amount of air to insure complete combustion and a slightly oxidizing atmosphere.

At the upper end of the wet-process kiln, chains are frequently suspended to aid in heat transfer and the exit gases often are employed to produce steam in "waste heat" boilers. The dust emerging with the exit gases is commonly precipitated in chambers, dust collectors, or electric precipitators. During the first World War, some cement plants recovered potash from this dust and sold it either as a fertilizer or as a refined salt. Cement dust, being basic, does not give rise to the lung disease "silicosis" which is caused by dust rich in quartz particles.

At the lower end of the kiln the clinker, which forms in rounded, sintered balls ranging from $^1/_8$ inch to over one inch in diameter, may be cooled and transported to storage or to the grinding mills in several ways.



A MODERN PORTLAND CEMENT KILN

These giant steel cylinders, lined with heat-resistant brick, may be upward of 400 feet in length and 12 feet in diameter. A rotary cooler, where the clinker is cooled, is shown below the kiln

The older practice was to allow the clinker to fall from the kiln onto a drag chain which carried it to the clinker pile, often under a sprinkling of water to aid in the cooling process. In most modern plants the clinker is now droppped into a cooler, of which numerous types

are used. Some of these are merely rotating cylinders passing the clinker counter to a flow of air, while others consist of moving grates through which air is blown. This hot air is then used with the fuel as a matter of economy.

Many chemical reactions occur during the progress of the charge through the furnace which entirely change the character and composition of the original materials. The raw material first loses water and, as it reaches hotter parts of the kiln, carbon dioxide is rapidly evolved from the carbonates of lime and magnesia. At a temperature of around 1280°C. (2336°F.), some of the fluxing constituents of the mix have reached a temperature where liquid is formed and from that point on interaction between the lime and the clay minerals is rapid. The liquid at this point consists largely of the alumina and iron oxide present, together with some of the lime and a smaller amount of silica. The compound dicalcium silicate, $2CaO \cdot SiO_2$, is formed and, as the temperature approaches a maximum, additional lime which is present combines with the dicalcium silicate to form tricalcium silicate, $3CaO \cdot SiO_2$. Both of these silicates are crystalline and may occur in the solid state at the high temperatures attained in the cement kiln. During the cooling process, but before the temperature has been reduced to the point of complete clinker solidification, the iron and alumina begin to crystallize out of the liquid with the remaining lime to form tetracalcium aluminoferrite, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, and tricalcium aluminate, $3CaO \cdot Al_2O_3$.

The magnesia present in the raw materials remains uncombined and is found in the form of periclase, MgO, in the clinker. The manner in which most of the minor components of cement emerge in the clinker has not been definitely ascertained.

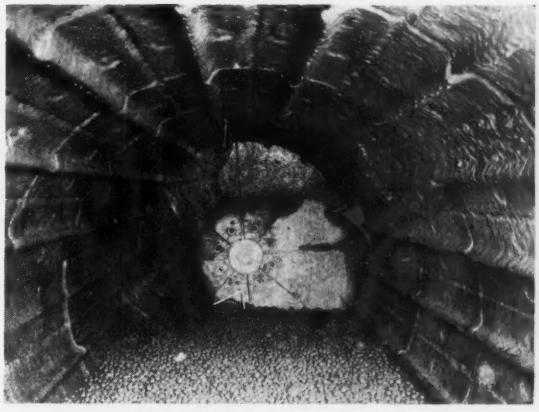
CLINKER COMPOSITION

If the clinker were to cool very slowly from the highest temperature attained down to the point of complete solidification, all of the liquid phase would crystallize and the clinker would consist substantially of the compounds above enumerated. In commercial practice, however, the cooling usually is too rapid for such crystallization to be complete; some of the liquid is undercooled and accordingly solidifies as a glassy phase. The range in glassy phase content of 22 commercial clinkers, as determined by a heat of solution method, was found to be from 2 to 21 per cent, with an average value of 6.8 per cent.

Although the composition of cement clinker may vary rather widely, depending on the type of cement, a typical phase composition may be given as follows:

	Per cent
$3CaO \cdot SiO_2$	52
$2CaO \cdot SiO_2$	22
$3CaO \cdot Al_2O_3$	7
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	7
MgO	2.5
Uncombined CaO	0.8
Minor constituents	1.6
Glass	7

Various solid solutions are known to be formed in limited degree so that the compounds given above cannot be considered, in commercial clinker, to represent pure phases but rather the basic compositions in which small amounts of other molecular groups may be dissolved.



INTERIOR OF A BALL MILL

These mills are used for pulverizing the clinker which, with a small amount of gypsum, results in portland cement. They are lined with armor plate and are partly filled with steel balls

The reaction taking place at the highest temperature is that by which CaO combines with $2CaO \cdot SiO_2$ to form $3CaO \cdot SiO_2$. If this reaction is not complete, uncombined lime will remain and the clinker is said to be "underburned." For reasons given later, uncombined lime in amounts greater than about one per cent is not permitted in modern cements, hence meticulous care is necessary to insure complete burning. A test has been developed by which the uncombined lime in clinker may readily be determined. This is based on the dissolving of the uncombined lime in a hot solution of glycerol and alcohol and the subsequent titration of the dissolved lime with an alcoholic solution of ammonium acetate. The reaction is as follows:

$$CaO + 2CH_3COONH_4 \rightarrow (CH_3COO)_2Ca + H_2O + 2NH_3$$

Other methods which have been found useful for gaining an insight into the degree of burning are the microscopical examination of the clinker and the measurement of the relative density of the clinker. The density increases as the reactions approach completion.

If the clinker were finely pulverized and this powder mixed with water and aggregate for making mortar or concrete, the paste often would be found to set or harden so rapidly that it could not easily be placed in the necessary forms before it would stiffen so as to be unworkable. To remedy this difficulty of premature stiffening, gypsum ($CaSO_4 \cdot 2H_2O$) is commonly ground with the clinker in amounts to give $1\frac{1}{2}$ to 2 per cent SO_3 in the finished cement. Thus, portland cement is the finely pulverized clinker described above to which has been added during grinding this limited amount of

gypsum and perhaps a very little water or other material to aid in the grinding process.

HYDRATION OF CEMENT

The ultimate purpose of portland cement is in the fabrication of concrete which results from the interaction of the cement with water in the presence of the sand and gravel or crushed rock. The aggregates take no essential part in the process but become bound into a rocklike mass by the reactions which occur in the paste of cement and water inclosing them. These reactions constitute the "hydration" of the cement. Obviously all operations bearing on concrete making must be concerned with these reactions.

In research on portland cement hydration it is sound procedure first to determine the nature of the individual compounds or phases that may exist in the clinker and then to prepare those compounds in the pure state and study their behavior separately. In this way it has been learned that tricalcium silicate reacts with water rapidly, forming an amorphous calcium silicate hydrate, having the approximate composition $2CaO \cdot SiO_2 \cdot nH_2O$, and crystalline calcium hydroxide, $Ca(OH)_2$. The amorphous calcium silicate hydrate, acting as a binding agent, develops its strength rapidly.

The dicalcium silicate, on the other hand, hydrates very slowly, giving the same calcium silicate hydrate but no measurable quantity of calcium hydroxide. In this case the strength is developed very slowly. Also it has been shown that the finer these silicates are pulverized the more rapidly will they hydrate and develop their strength. Some years ago it was necessary to allow concrete highways to harden with applications of water (known as the curing process) for twenty-one days before they could be opened to traffic but by

THE PENNSYLVANIA TURNPIKE OVERLOOKING EVERETT, CUMBERLAND COUNTY, PENNSYLVANIA

This concrete dual-lane highway, with no grade crossings, is typical of the express highways that are now attaining wide interest throughout the country

taking advantage of the principles just mentioned—that is, increasing the tricalcium silicate content at the expense of the dicalcium silicate, and grinding somewhat finer—it has been possible to reduce this time period for regular cements to seven days. By going still further in these directions and controlling the product more closely, there has been put on the market a type of portland cement known as "High Early Strength" cement, which will produce concrete that can be opened to traffic in two or three days.

This example is illustrative of the advances in the engineering art of concrete making that may be brought about by an application of chemical knowledge regarding the constituents of cement. When Boulder Dam was to be built the masses of concrete contemplated were of such size that it was necessary to introduce methods for avoiding the high temperatures that otherwise would result from the hydration reactions of the cement. Research had shown that the compound tricalcium aluminate was responsible for the largest amount of heat evolution, this compound reacting rapidly with water to form tricalcium aluminate hexahydrate, $3CaO \cdot Al_2O_3 \cdot 6H_2O$. The next worst offender in that direction was tricalcium silicate, the hydration of which has been described. Consequently, a cement was designed to consist of a minimum of $3CaO \cdot Al_2O_3$ and having a low limit on $3CaO \cdot SiO_2$. The product, known as "Low Heat" cement, evolved much less heat during hardening than ordinary cement and was used in Boulder Dam and in many other similar structures. The disadvantages attendant upon the slow rate of hardening of Low Heat cement, due to its low $3CaO \cdot SiO_2$ content, led to the development of an intermediate type which is known as "Moderate Heat" cement. In this the $3CaO \cdot Al_2O_3$ content is limited but to a lesser degree than in Low Heat cement. This product has found extensive use in the structures of the Tennessee Valley Authority.

Concrete is sometimes exposed to the action of soil waters high in certain salts, such as sulfates, and research has shown that, of all the compounds of cement clinker the $3CaO \cdot Al_2O_3$ is by far that most rapidly attacked by sulfate solutions. Consequently, a type of cement has been developed of very low $3CaO \cdot Al_2O_3$ content and this is known as "Sulfate Resisting" cement.

SPECIFICATIONS AND TESTS

Thus research on the reactions of the cement compounds with water has led to the development and recognition of five types of cement, the latter four of which are designed for particular types of service. All of these cements, however, to be acceptable must meet certain standard specifications as indicated by the American Society for Testing Materials, the Federal Specifications Board, and other large groups such as the state highway commissions, water boards, Reclamation Bureau, and Army Engineers.

Tests are included to eliminate cements containing an excess of uncombined lime (underburned clinkers) and an excess of magnesia, because the presence of those oxides above certain limits brings about an unsound condition in concrete structures. This is due to

expansions resulting when those oxides react with water to form $Ca(OH)_2$ and $Mg(OH)_2$, respectively.

The specifications include tests to insure a proper working period, measured by a limit on the time of initial and of final set. This is insured by the addition of the proper amount of gypsum during manufacture. If no gypsum were added to pulverized clinker, the crystalline $3CaO \cdot Al_2O_3$ would react with the added water very rapidly, as stated above, to form tricalcium aluminate hexahydrate. The structure developed by this paste would become rigid in a few minutes and further working and placing would be difficult or impossible. Gypsum, $CaSO_4 \cdot 2H_2O$, prevents this, by combining with most of the tricalcium aluminate.

Difficultly soluble calcium sulfoaluminate is produced by the following reaction:

$$3(CaSO_4 \cdot 2H_2O) + 25H_2O + 3CaO \cdot Al_2O_3 = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$$

The formation of this compound, by the principle of the Mass Law, keeps the concentration of the aluminate in solution below that at which $3CaO \cdot Al_2O_3 \cdot 6H_2O$ can separate. This condition prevails until the $CaSO_4$ or the $3CaO \cdot Al_2O_3$ is exhausted or the $3CaO \cdot SiO_2$ has progressed in its hydration to a degree where the free water is inadequate to maintain fluidity and the paste stiffens or "sets." In this manner the gypsum functions to "retard" the set, and to allow the set to be governed by the hydration of the $3CaO \cdot SiO_2$.

The specifications include tests on tensile or compressive strength of specimens made in accordance with a prescribed procedure and tested at specified ages in order to insure that the structures built are adequate to support anticipated stresses. In the case of the low heat, moderate heat, and sulfate-resisting cements, the specifications also include tests to insure that proper chemical compositions are embodied in those cements to meet the special requirements.

A modified portland cement sometimes is produced by the introduction, during grinding of the clinker, of an active siliceous material, designed to aid in the bonding action by interacting with the calcium hydroxide formed during hydration of some of the cement compounds. Such materials were used by the Romans and are extensively employed in Europe. These materials consist of natural volcanic deposits, known as puzzolanas, tuffs, trass, shales calcined or uncalcined, or slags, and the mixtures with the portland cement are variously known as trass cements, eisen cements, slag cements, or puzzolan cements.

THE "PLASTIC" CONCRETE

In the fabrication of concrete, all of the benefits coming from the use of a perfectly suitable cement may be lost by a lack of recognition of the structural effects in the paste brought about by interaction with water. The use of an amount of water in excess of that required to form dense paste or the use of a gradation of aggregates that will result in segregation or honeycombing will discount any benefits due to the use of an ideal cement. Concrete is made where it is to be used, or near there, and is not subject to the control of the cement manufacturer. Because of improper knowledge

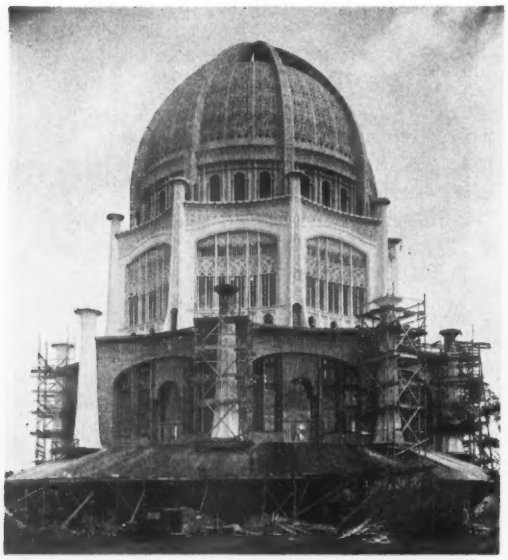
MODERN APARTMENT HOUSES IN ARCHITECTURAL CONCRETE

of the requirements of the plastic paste of the right water/cement ratio, of the right consistency, of the right gradation of aggregate, and the proper curing, disappointing results sometimes have been obtained in concrete structures.

This aspect of the problem constitutes the art of concrete fabrication. Ceaseless attention to detail in the application of a real understanding of the chemical processes of concrete making is necessary to insure durable concrete. The amount of water added must be adequate but must not exceed that required to make a workable "grout." This can be much less if the concrete is subjected to high-frequency vibration than if placed by hand. Any excess of water expands the paste structure, unless removed prior to set, and so reduces the strength of the member. But once the grout has set, water must be kept on it to permit the reactions of hydration to proceed as far as possible and to prevent the evaporation of water from the paste. Loss of water before adequate hardening may cause a cracking of the surface layers.

For special purposes, small amounts of organic or inorganic substances, spoken of as admixtures, are sometimes mixed with the concrete. These may be used to enhance water repellency of the structure, to accelerate hardening, to improve impermeability, or

to produce a road slab that will resist the deteriorating effects of an oft-repeated cycle of freezing and thawing



THE BAHA'I TEMPLE AT WILMETTE, ILLINOIS, UNDER CONSTRUCTION

This shrine, fabricated with white quartz aggregate, is a magnificent example of the structural beauty that may be produced with concrete

or the effects of salts which may be used on highways to melt the ice during the winter months.

The aggregate employed in mortars is a fine sand, but in concrete a gradation is employed with maximum size of rock or gravel depending on the size of the member in which it is to be employed. For the making of good concrete, the aggregate must be properly graded so that no pockets of any size remain and the cement paste bathes each separate grain. All aggregates must of course be durable and not subject to disintegration.

When these principles are meticulously carried out concrete becomes, in the hands of an artisan, a plastic rock possessing all of the virtues of the natural building stones but embodying in addition the tremendous advantages that it can be cast in any size or shape desired, that it can be poured in place or molded in the shop, that it may be given any color or tone by the use of colored aggregates or mineral pigments, or any texture by the use of the mason's art. The old-time concrete building of uninteresting form, unadorned, and of muddy gray color, is a structure of the past. Today great edifices of marked beauty meet the eye in every city—churches, schools, hospitals, hotels, office buildings—where the "plastic" concrete has come into its own. Nowhere is there a more beautiful shrine than the Baha'i Temple in Wilmette, as conceived by Louis Bourjois and produced by John Early—"A shelter of cobweb interposed between earth and sky, struck through and through with light." But this plastic is not confined to the great buildings, large dams, magnificent highways, and city pavements. In the past five years there have been upward of 100,000 homes of one type or another constructed of concrete, bridges of endless design and viaducts by the thousands, airport runways, railroad beds, gasoline storage tanks, silos, feed pens, water and sewage conduits,. . . .

Thus has research upon portland cement contributed in this industrial age to the satisfactions of life.

What's Been Going On

Phosphorus Concentration in Steel Showed by Radioactive Tracers

THE concentration of phosphorus on the surfaces of the little air pockets or blow-holes in iron or steel has recently been proved by using radioactive tracers, according to Westinghouse research physicist W. M. Shoupp. Keen interest in this subject comes from the fact that too much phosphorus makes steel brittle, and the more that can be determined about the way these two substances combine with each other, the greater the opportunity to improve steel making.

A simple "camera," consisting of a tin can, two small brass discs, and a screw clamp, was improvised for this experiment. This device records on photographic film the rays from artificially radioactive tracers of phosphorus, revealing their location in the steel.

This simple method of taking pictures of radioactive tracers can be used to reveal the location of other substances besides phosphorus. For example, steel also contains small amounts of sulfur, carbon, manganese, and silicon. Any of these substances can be made into tracers with an atom-smasher.

A sample batch of steel was melted into which were put radioactive atoms, or tracers, of phosphorus. The phosphorus had been made artificially radioactive by bombardment in an atom-smasher, so it would send out invisible rays like those emitted by radium. These rays do not affect the action of the phosphorus, but they reveal the location of the atoms from which they are sent out.

A small disc of steel was molded containing the tracer atoms. In a dark room, a piece of photographic film was laid on each side of the steel disc, two small brass plates were placed outside the film, the stack of film clamped, and the whole thing placed in a tin can to keep out all light.

The developed film revealed blotches caused by the rays from the phosphorus tracers. The light areas on the print corresponded with the blow-holes in the steel disc, indicating that the phosphorus had concentrated on the surfaces of these holes.

John Maclean, Charles Macintosh, and an Early Chemical Society in Glasgow

J. A. V. BUTLER[1]

University of Edinburgh, Edinburgh, Scotland

THE earliest society devoted specifically to chemistry of which we have record is one composed of pupils of Dr. Joseph Black, which existed in Edinburgh in 1785. Little is known of this Society, except a list of members, an account of which has been given by Kendall (*1*).

In the Memoir of John Maclean, M.D., by his son (*2*) there is a statement that he was a member of a chemical Society in the University of Glasgow. John Maclean was born in 1771 and entered the University of Glasgow at the age of 13. The writer of the Memoir states that Dr. Maclean read at least seven papers before this Society, one of which, dated March 29th, contains a reference to Dr. William Irvine of Glasgow, who died in the summer of 1787. The paper was certainly written before this time and the writer of the Memoir considers it probable that the date was March, 1786, when the author was 15.

After leaving Glasgow John Maclean studied with Dr. Black in Edinburgh and went to London and Paris. He then returned to his native city and practiced his profession for a year. He emigrated from Scotland in 1795 and became Professor of Chemistry in the infant College of New Jersey. His career has been described in a number of articles (*3*).

The writer of the Memoir says that

"at the University he was, while yet a lad, a member of the Chemical Society, a club which appears to have met at the University, with the permission of the College authorities, if not under the oversight of the Professors. The members submitted, for the consideration of the Society, papers and essays upon various matters connected with the object of their association, and some of these papers seem to have foreshadowed the eminence which the authors of them attained in after life, as proficients in the art of Chemistry."

Of the papers of John Maclean the writer of the Memoir reports that

"One of these was on *respiration*, another on *fermentation*, and another on *alkalies*. The subjects of the others are unknown to the writer of this memoir. Dr. Maclean's papers on *fermentation* and *alkalies* are now in the possession of his son, Dr. George Macintosh Maclean."

A large collection of the papers of the Maclean family has recently been added to the Princeton University Library, including the papers of George Macintosh Maclean. The writer has looked through many of these and examined the list of them, but was unable to find any trace of the papers mentioned above. The collection, however, contains records of some lectures of a later date.

More information about this Society is to be found in the Biographical Memoir of the late Charles Macintosh, F.R.S., of Campsee and Dunchattan, by his son George Macintosh (*4*). This Charles Macintosh was the inventor of the waterproof coat which bears his name and was one of the leading pioneers of industrial chemistry of his time.

Born in 1766 at Glasgow, this energetic young man before he was twenty embarked on the manufacture of sal ammoniac from soot and animal and vegetable offal, a process which had been carried on by Baumé in France until 1787. It was continued at Glasgow from about 1786 to 1792. He introduced the manufacture of sugar of lead into Britain from Holland when only 20 years of age. About the same time he discovered how to make aluminum acetate and introduced it as a mordant in calico printing.

His later activities, which would take too much space to describe here, include a method of preparing dry chloride of lime and its introduction into bleaching practice, the establishment of an alum factory near Glasgow (1797), manufacture of prussian blue and of prussiate of potash, and his patented process (1822) of waterproofing clothing with solutions of caoutchouc in naphtha, then produced as a product from gas works.

Charles Macintosh was also a member of the Glasgow Society in or before 1786 and the Memoir gives us some further information concerning it. He read papers to the Society on the following subjects:

On the Application of the blue colouring matter of Vegetable bodies
On Alcohol
On Alum
On Crystallization

These foreshadow in a striking way the interests of his later life and the passages which are quoted show that at least he was well abreast of the scientific thought of this time. For example, we may quote the following from the first-named Essay.

"He next describes the method of dyeing with indigo, and overthrows the theory of Mons. Hellot, that the blue colours of indigo-dyed cloths was owing to the adhesion of vitriolated tartar to the cloth, seeing that this salt is soluble in water, whilst indigo blue is fixed. He also overthrows Dr. Irvine's theory, that the gummy particles of indigo, when changed into resins by the process of dyeing, and becoming thus unsoluble in water, remain as fixed colours upon the cloth, by showing that these resins are all soluble in spirits of wine; and would, by the application of such spirits, be discharged from indigo-dyed cloth, whilst in reality they are not. He then argues that the salts used in the indigo

[1] Present address: 4620 Norwood Drive, Chevy Chase, Maryland.

vat become chemical components by the colouring matter, and that in its turn this compound enters into chemical union with the cloth dyed, which compound is insoluble in water."

This seems admirable in content, in scientific approach, and in a healthy spirit of dissent from the views of his teacher.

In the autumn of 1786 Mr. Macintosh undertook a mission to the Continent with the double object of introducing the use of cudbear (a pigment obtained from lichens) and of selling sulfuric acid made by the Prestonpans Vitriol Company. While he was there William Couper wrote as follows:

From William Couper, Esq., to Charles Macintosh, Esq., (then in Holland)

Glasgow, December 14th, 1786

My dear Sir,—I had the pleasure of your letter dated at Rotterdam some time ago. Some convulsions in our society, which are now happily over, induced me to put off writing until I saw their termination. Owing to a regulation of the College Faculty, every society existing within the College was under the necessity of acquainting the Principal with the nature and intention of their meetings, and of sending him a list of the members. This, though it appeared to most of us a thing simple, and easy, to be submitted to, had a different effect on others; and we lost Mr. Candlish, Mr. Tilloch and Mr. Crawford. In other respects, we, I think, flourish; and, I doubt not, will continue to do so.....

Believe me, my dear Sir,
Yours, most sincerely
Wm. Couper"

In the following year we find Dr. Eason of Manchester writing, from which I extract the following, which includes some interesting remarks concerning Dr. Irvine's effects.

Manchester, 18th October, 1787.

Dear Charles,—I begin on a large sheet without hopes of filling it. I had a letter from Dr. Black yesterday. He laments the death of Dr. Irvine, very much. Pray, what does Mrs. Irvine intend to do with the museum and MS. lectures? My life for it, they will sell well. I think we could dispose of twenty copies here, near as many in Liverpool, and London would take off many hundreds. Every F.R.S. who has any idea or knowledge of chemistry would take a copy.....

How does your chemical society get on? I am afraid, badly, since poor Irvine is gone. However, you must keep it up. We intend another volume of our transactions by next spring. I am out of the scrape, and shall continue so till the end of the chapter.

Yours, ever
A. Eason.

Of the members of the Society mentioned in the above letters, Mr. Candlish was a student of divinity, the father of Dr. Candlish, a celebrated Free Church character; Mr. Tilloch (1759–1825) invented stereotyping (1784) and a method of printing bank notes (1790). He went to London in 1787 and in 1797 established the *Philosophical Magazine*. William Couper was a partner of Macintosh in the ammonia project and later an eminent surgeon in Glasgow.

Other members mentioned in the Macintosh Memoir are Mr. John Wilson, of Hurlet, and Major Finley, Royal Engineers. These both became partners with Macintosh in the Hurlet alum works. The Maclean Memoir also names as members Mr. Cruikshank, Mr. Archer, and Mr. Monroe, about whom nothing has been found.

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(3) FOSTER, "Doctor Maclean and the doctrine of phlogiston," J. CHEM. EDUC., **2**, 743 (1925); FOSTER, "Some letters by Doctor John Maclean," *ibid.*, **6**, 2104–14 (1929); DAINS, "John Griscom and his impressions of foreign chemists in 1818–19," *ibid.*, **8**, 1288 (1931); *Science*, **60**, (Oct. 3, 1924).
(4) "Biographical memoir of the late Charles Macintosh, F.R.S., of Campsee and Dunchattan," compiled and edited from authentic documents by his son GEORGE MACINTOSH, printed for private circulation by W. G. Blackie and Co., Villafield, Glasgow, **1847.**

THE FRANKLIN INSTITUTE EQUIPMENT FOR CHEMISTRY DEMONSTRATION

R. D. Billinger and Lester Kieft showing spectacular reactions in connection with the Engineering Defense Training course

NOTICE TO AUTHORS

ATTENTION is called to the fact that there appears in this number the usual Notice to Authors, which will be printed hereafter in the first issue of each year.

• Copies of the *Proceedings* of the Fifth Annual Southern Conference on Audio-Visual Education, which was held in Atlanta on November 13–15, 1941, are available for purchase at one dollar each. Included in the *Proceedings* are the principal addresses given at the Conference, and complete stenographic transcripts of seven group forums which were conducted during the Conference by leading audio-visual educators. Orders and remittances should be sent to the Southern Conference on Audio-Visual Education, 223 Walton Street, N. W., Atlanta, Georgia. Postage is free on all orders which are accompanied by remittances.

High-School Chemistry

An Experiment in Chemistry Teaching

J. HERBERT WARD *Classical High School, Providence, Rhode Island*

IN THE November, 1941, issue of this JOURNAL this sentence appears: "In fact, those pupils who have studied elementary chemistry or physics in school, preferably with self-performed laboratory experiments, have a favorable rating with employers." From another source this claim was made: "Science today dominates the world . . . the world will need an increasing number of people trained in science."

Yet in many secondary schools the teachers of chemistry, in particular, have seen two laboratory periods changed to one and the money available for chemicals reduced again and again. Or they are asked in one year to offer a course adapted for pupils not going to college as well as for those who are.

We at the Classical High School in Providence, faced with this perennial dilemma, became convinced a decade or more ago that, unless we were willing to sacrifice individual laboratory work by the pupils themselves, there was no solution. Individual laboratory work has been eliminated in many places, especially since many chemistry teachers have such extra duties as charge of a home-room, which make it impossible to prepare laboratory experiments properly in the time at their disposal. The colleges still insist on such individual work, as do the employers evidently. We felt we did not want to sacrifice this laboratory experience for students for the reasons cogently expressed by Stuart Cushing, present head of the department of science at East Boston High School:

1. The pupils like it and therefore will do something wholeheartedly, thoroughly, and will learn more.
2. Pupils acquire skill in handling tools and apparatus transferable to any kind of work they may do in later life.
3. When pupils are taught to observe carefully, seeking every little cause and effect, they tend to become analytically minded.
4. Pupils learn that they must be careful to obtain accuracy.
5. Individual laboratory experiments teach the need of absolute honesty in all work in science.

Having decided to meet honestly the College Entrance Examination Board requirements in this respect, the problem was then to chart a course that would be valuable for any purpose and which would still meet the demands for those who intended to continue with chemistry in college. First, the mechanics of the curriculum had to be studied. It was obvious that a two-year course was out of the question, especially in a classical high school. But, if we offered a year's course for school credit and a one-and-one-half year course for college certification, and also a similar plan for physics, there would be no difficulty in arranging programs. So it was decided that, after the usual eleventh year work of five periods a week in chemistry, those wishing to do so would continue for one-half year five days a week, and then finish the year with a similar semester course in physics.

But there still remained the question of content of each part of the course. Fortunately, there appeared in April, 1936, in this JOURNAL (page 175) a one-year course in chemistry for secondary schools recommended by a board composed of science teachers from all over the country. This was modified so that in the one-year course 30 experiments could be performed by the students, all subjects but the metals and the so-called optional topics in organic chemistry could be studied, the writing of equations, including those in ionic form, and the solution of problems (except those involving normal or molar solutions or equivalent weights) could be mastered.

Then, those caring to specialize in chemistry enter the half-year course knowing the mechanics of equations and problems. They have a certain skill in laboratory technic, and are ready to perform ten experiments of a quantitative nature and those introducing the student to Group I of qualitative analysis. Metals, optional organic subjects, and the problems previously omitted are now considered. The entire field previously studied is reviewed, emphasis being placed on topical presentation of all topics instead of the customary recitation. As a result, our students are usually able to omit the introductory course in chemistry in college.

After forty years of teaching under all kinds of conditions, and after trying various methods of solving the dual problem of preparing for life and for college chemistry courses, we are convinced that the above solution is the best approach. It embodies the aims of such a course as that described in an address by Professor R. A. Baker, of the College of the City of New York, before the New England Association of Chemistry Teachers in September, 1936:

"The development of a sense of matter-reliance upon the properties of substances which determine their responses to their environment; expectancy of changes which will produce new substances with new properties; mastery of the controls which man can exercise over these changes; a vocabulary which will enable the student to read intelligently chemical news in the daily press; sufficient technical knowledge to enable the student to interpret phenomena, appreciate the chemical foundations of industry, and vote intelligently upon such public questions as the purification of water, the disposal of waste, air conditioning,

and the preservation of food; a vision of the fields of chemistry for those who have not yet found themselves, and at the same time a barrier to discourage those who are unfitted to enter the profession; perseverance, originality, independence, initiative, confidence, and accuracy developed by individual laboratory work."

Out of the Editor's Basket

A STUDY by R. W. Burnett (published in the *Teachers College Record*) cited the results of a questionnaire to show that four-fifths of the elementary and secondary-school teachers believe that it should be one of the functions of science education to deal with unsolved problems and the important sociological and political issues of a controversial nature in which science has something worth while to offer. Nevertheless, science teachers indicate that they are avoiding the problems which they themselves think the most important, principally from fear of official disapproval, lack of sufficient knowledge, and from the feeling that students are too immature. A recent study by the National Education Association is said to have shown that 67 per cent of the general public favors the discussion by teachers of current controversial issues and it is implied that opposition would very likely disappear if the public were assured that discussion would be fair, critical, and intelligent.

● There is still a good deal of interest in the operation of the Selective Service System as it affects the younger members of the chemical profession. While it has been clearly stated that the intention is to keep chemists in positions where they can make use of their training and experience, there is nevertheless some concern over the efficiency with which the official machinery accomplishes that result. Francis J. Brown, in an address before the Association of Colleges of Pharmacy, discussed this question. Dr. Brown, of New York University, has been loaned to the government service at the request of the American Council on Education for the express purpose of handling the problems created by national defense, including Selective Service, as they affect the students in colleges and universities.

He said that while there is still some divergence of opinion among the six and a half thousand local boards, as regards their attitude toward deferment of military service, there is a growing uniformity of practice among them. This has been the result of the efforts of the national headquarters of Selective Service in seeking continually to call to the attention of the boards those areas in which there is a definite demand, in the interests of national defense, for continued training of individuals.

He cited a case in which a local board had refused an application for occupational deferment, contrary to the policy of the national headquarters. The appeal board had confirmed this judgment. National headquarters informed the state director by telephone of this action, explaining the case in full. In two days the decision had been reversed and a student was allowed to complete his training.

A college president proudly announced that his institution was 100 per cent loyal to national defense since it had not made a single request for occupational deferment of a student. It was difficult to point out to him that this attitude was a mistaken one and not in the true interests of defense. Pursuing this question further, Dr. Brown said:

"The first responsibility for making selective selection rests with you who are the administrators in the colleges and universities, and if that attitude of coöperation can be established, I have little doubt but that the problem of the professional school is one that has been solved almost completely. One institution, a very large university, reported to me only last week that the first weeks of July about 60 per cent of the students for whom they had requested occupational deferment were receiving such deferment from local boards. Last week they brought that report up to date and today 89 per cent of their requests for deferment are being recognized by the boards, primarily I think because the institution has set up the machinery to make this first initial combing of recommendations for deferment. . . ."

Even in cases in which occupational deferment is not claimed there is provision by which students can complete their immediate periods of study if called for induction. The provision for postponement of induction "because of unusual personal hardship" was said to have been written primarily for the college student. This postponement can be for a period of sixty days, with the possibility of renewal. To make such requests regularly for a semester, and for seniors and graduate students for an entire year, will accomplish administratively the purpose which would otherwise be accomplished by legislation.

Dr. Brown summed up the present situation as follows:

"The general public, I think it can be said, have frankly recognized these various contributions of colleges and universities to national defense. There has been no resentment of the occupational deferment of men in these essential professional areas. The danger lies not as I see it with public opinion but within the colleges themselves, in those who in their eagerness to serve immediate defense needs lose sight of this long-range function of their own institution. In these days it is neither dramatic nor spectacular to go on doing a good or even a better job of the same thing that we have been doing. Colleges and universities seek only to serve the national interests. They can do this best only by keeping continually before them their twofold objectives: seeking in every way possible to meet immediate defense needs but seeking at the same time to continue to meet on a high standard the long-range needs of professionally trained personnel. Neither of these two objectives can be lost sight of,

Editor's note: Since this was written the situation has of course changed so radically that it is a question whether much of the above discussion is any longer pertinent.

even in our enthusiasm for movement or because of the gravity of the present situation, without irreparable loss to the nation and at the cost of future security of our welfare and of our people."

● The following extract from *Chemical News*[1] was brought to our attention recently and we pass it on by way of diversion. It must be remembered that the Type Theory of valence was in vogue in 1865, which accounts for the nomenclature and the notation used in the formulas. Apparently an "ammonia system of compounds," later highly developed by E. C. Franklin, was being thought of even then.

WATER FROM A MANIACAL POINT OF VIEW

To the Editor of the Chemical News: Although the madmen here who have got me and a number of other perfectly sane individuals under their charge will not allow me the use of chemicals and apparatus, my brain works as actively and as clearly as if I had the Royal Institution laboratory at my disposal. I have just made a most important discovery, which I lose no time in communicating to you.

I have discovered that water is a member of the already large tribe of ammonias. If we take the compound atom

$$N'''\begin{cases}H'\\H'\\H'\end{cases}$$

as a typical basis, nothing is easier than to replace the triatomic atom N''' by the monatomic atom H' and the diatomic atom O'', we then replace one of the H's by the monatomic radicle HO, and the thing is done. Water must, therefore, henceforth be formulated thus:—

$$\begin{matrix}H'\\O''\end{matrix}\begin{cases}HO'\\H'\\H'\end{cases}$$

and must be called *dihydrohydorylhydroxamine*. Hydrate of potash will be—

$$\begin{matrix}H'\\O''\end{matrix}\begin{cases}HO'\\K'\\K'\end{cases}$$

dipotasshydorylhydroxamine. Of course the H' and O'' on the left side of the bracket exist in a state of combined separation, or separate combination, which allows them to perform triatomic functions.

I am now hard at work on marsh-gas, which, I have no doubt, I shall also shortly be able to prove to be an ammonia.

Yours ammoniamaniacally,
N. H. THREE

Hanwell

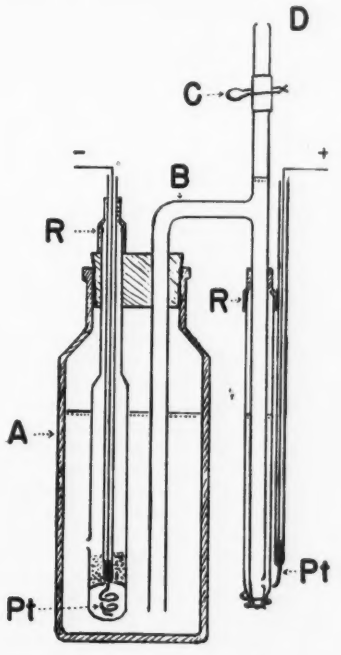
● The current reports in the newspapers remind us that we have been receiving reports from the Department of Science of the Ministry of Economic Affairs of Thailand. We were astonished to see the amount of chemical activity which this tiny country supports. Much of it apparently has to do with the pharmaceutical chemistry of tropical drugs, but there has also been added recently an active division of ceramics.

● Among the interesting and valuable bits of "free literature" available for science instruction we are glad to call attention to "The Story of Lightning," a pamphlet issued by the General Electric Company.

[1] *Chem. News*, 12, 206 (1865).

● E. Edward Johnson, of Omaha, Nebraska, describes a method of making glass beads. A piece of glass rod is drawn out to the diameter desired for the glass beads. The rod is then heated red hot over a Bunsen burner placed on a heat-resistant desk top. The end of the rod is then clipped off by means of an old pair of scissors, the glass rod falling to the table. These beads can be cut in the shape of a rectangle, square, or tetrahedron and may be used to prevent bumping when boiling.

● T. Asami, of Michigan State College, sends us the accompanying illustration of a simple calomel electrode. It consists of a four-ounce bottle, *A*, which serves as a reservoir for the KCl solution. This contains the calomel electrode, with calomel, mercury, and platinum wire connection as shown. The side arm *B*, leading to the immersion electrode, is inserted in the large rubber stopper *sideways*, through a notch, to avoid contamination of its lower end with rubber. The inner tube of the immersion electrode is *ground* into the outer jacket at the lower end. The positive platinum electrode is coiled around the tube at this point. Suction is applied at *D* to fill the apparatus with KCl solution, including the inner and outer tubes of the immersion electrode. When not in use the clamp *C* is released



CALOMEL ELECTRODE

and the solution drains into the reservoir, so there is no subsequent loss by diffusion through the ground joint. Rubber connections are shown at *R*. The platinum wires are either sealed or cemented into the glass tubes.

RECENT BOOKS

CATALYSIS, INORGANIC AND ORGANIC. *Sophia Berkman, Jacque C. Morrell,* and *Gustav Egloff,* Universal Oil Products Company, Research Laboratories. Reinhold Publishing Corporation, New York City, 1940. xi + 1130 pp. 75 figs. 15 × 23 cm. $18.00.

In the one volume CATALYSIS the authors have gathered together a relatively enormous amount of factual material, drawn from the whole field of catalysis and covering the period from the present back over many years. Because of the considerable divergence of opinion with respect to the mechanism of catalysis and to the interpretation of experimental data the authors have preferred "to arrange the findings of the various workers in the field and their original interpretations into a systematic presentation of the subject with some consideration of its historical evolution." Thus the presentation is encyclopedic rather than critical.

The book is divided into eleven main chapters with appended bibliographies, and is well indexed as to subjects and authors. The chapters are devoted to the following subjects: The Phenomenon of Catalysis; Adsorption and Catalysis; Heterogeneous and Homogeneous Catalysis; The Activity of the Catalyst; Inhibitors in Catalysis; Promoters and Poisons in Catalysis; Carriers in Heterogeneous Catalysis; Catalytic Reactions in Inorganic and Organic Chemistry; Physical Conditions in Catalytic Reactions; Classification of Catalysts with Respect to Type of Reaction; Catalysis in the Petroleum Industry. Very extensive use is made of tables in a systematic presentation of facts, so that even though the book is large, its data are readily available. "It is the belief of the authors that future research in the field of catalysis may be logically derived from the systematically presented facts instead of from the empirical methods used at present." The authors have made an important contribution to the literature of catalysis and have created a source book to which all those interested in the catalytic field will wish to have access.

W. W. RUSSELL

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QUALITATIVE ANALYSIS AND CHEMICAL EQUILIBRIUM. *T. R. Hogness* and *Warren C. Johnson,* University of Chicago. Revised Edition. Henry Holt and Company, New York City, 1940. xvi + 538 pp. 33 figs. 14 × 23 cm. $2.90.

The revised and expanded edition of this textbook is exactly what would have been expected as a development from the well-planned and well-written first edition [reviewed in J. CHEM. EDUC., **14,** 448 (1937)]. As in the earlier edition the methods of presentation are matter-of-fact and the literary style is simple. Any teacher of qualitative analysis will find this text to be stimulating and to contain very worth-while suggestions for presenting chemical equilibrium to students of qualitative analysis.

The new book is larger (by approximately 120 pages) and the revision is extensive. Many sections were entirely rewritten and extensive insertions were made in all but a few of the chapters. Chapter 1 includes a more extensive discussion of the nature of ionic structure. Chemical equilibrium is the main theme for Chapters 2 to 9. The Brønsted concept is emphasized in Chapters 2, 6, and 8. The compilation of questions and problems which illustrate the various principles outlined in each chapter serves to summarize and emphasize the principles discussed. A study of these problems should definitely clarify the relationships existing between the theory of qualitative analysis and the laboratory phase of the course. This interesting and very useful part of the text includes the first 271 pages. (This part of the book is reprinted as a separate text. See next review.)

The more significant changes appear in the Experimental Part, or Part II of the text. Whereas the first edition utilized essentially a small-scale adaption of the Fresenius scheme of qualitative analysis, the second edition includes this procedure presented as schemes for use either with centrifugation or with small filters and funnels. Important changes in the procedure involve the separation of the cadmium and cupric ions by the use of cadmium chloride complex ions to decrease the cadmium ion concentration sufficiently to present the formation of cadmium sulfide; the use of hydrogen peroxide to oxidize stannous ion to stannic ion; the use of the bisulfate ion as a weak acid for use as a buffer solution in the Group III analysis; and a separation of strontium and calcium based on the acidic nature of the bisulfate ion.

The section on anion analysis has been improved and expanded. It is designed to encourage the student to use his ingenuity and his knowledge of both anions and cations. Throughout the text a very adequate number of chemical equations, tables of data, and other pertinent information for the solution of problems are given. The appendixes include, in addition to the expanded tables about reagents, a section on mathematical operations and tables of ionization and dissociation constants.

This second edition should prove to be more popular than the first.

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IONIC EQUILIBRIUM AS APPLIED TO QUALITATIVE ANALYSIS. *T. R. Hogness* and *Warren C. Johnson,* University of Chicago. Henry Holt and Company, New York City, 1941. vii + 306 pp. 23 figs. 14 × 23 cm. $2.00.

This text consists of the theoretical part (Part I, or the first 271 pages) and the appendix of the revised edition of QUALITATIVE ANALYSIS AND CHEMICAL EQUILIBRIUM. (See preceding review.) As expressed by the authors, "it is designed to meet the needs of teachers who either prefer to use their own particular scheme of analytical procedure or want to include in their courses supplementary material on chemical equilibrium in the form of problems and exercises."

This text should find wide application by teachers of qualitative analysis; the authors are to be commended for making available this material in the form of a separate text.

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ORGANIC SYNTHESES. Volume 21. *Nathan L. Drake,* Editor-in-Chief. John Wiley and Sons, Inc., New York City, 1941. v + 120 pp. 14.5 × 23.5 cm. $1.75.

This yearly publication gives the equations for the reactions, procedures with accompanying notes, and other methods of preparation of 38 different organic compounds, with formulas verified by competent referees. It is valuable for keeping up with new and satisfactory methods for the preparation of organic chemicals.

BIBLIOGRAPHY, A BEGINNER'S GUIDE TO THE MAKING, EVALUATION, AND USE OF BIBLIOGRAPHIES. *Marion Villiers Higgins,* Assistant Professor, Emory University Library School. The H. W. Wilson Co., New York City, 1941. 43 pp. 13.5 × 19.5 cm. $0.60.

As a brief introduction to the subject of bibliography in an attempt to cover the needs of first-year library school students, this is a general work and as such would be of help to a bibliographer of chemistry, but does not meet his problems specifically. The pamphlet is divided into four chapters discussing: definitions, types, functions, and objectives of bibliography; bibliographical form; evaluation of bibliographies; compilation of a bibliography.

THE SEPARATION OF GASES. *M. Ruhemann*. Oxford University Press, New York City, 1940. xiii + 283 pp. 148 figs. 16.5 × 24 cm. $5.75.

The liquefaction of the permanent gases began with the observation by Cailletet of a transient mist in a cooled capillary glass tube containing oxygen under pressure and subjected to sudden pressure release. This was in December, 1877, and almost at the same time the same phenomenon on a larger scale was observed by Pictet in Geneva. The application of the porous plug expansion cooling combined with the regenerative principle of Siemens by Hampson in England and Tripler in the United States was, however, the means by which liquid air was first produced in quantity. The present volume presents considerable detail about the theory underlying the three standard processes for producing oxygen that have grown to maturity since the original development of Carl Linde nearly fifty years ago.

Low temperature refrigeration, in spite of the relatively long existence of the means of producing liquid air, is in a somewhat primitive stage. For this reason, and also because of the already evident industrial importance of low temperature refrigeration, the author has collected and put into readable form a generous amount of information on the properties of mixtures of very volatile substances and the methods for their separation. The ever expanding role of oxygen in industry accounts in part for the author's four chapters on the methods and devices evolved for separating the constituents of air. For the rest, these plants serve as models to be followed in solving other problems of gas separation: for example, the constituents of coke-oven gas. From the point of view of general interest, the volume is very welcome. The engineer and scientific worker will find a very acceptable collection of material which has not previously been assembled.

The introductory chapter reviews the composition of coal gas, coke-oven gas, cracker gases, and natural gases from various world sources. One shudders to find that in addition to the wide range of rigors to be endured in the U.S.S.R., liquid methane can be dispensed from tanks. The critical temperature of methane is −81°C.!

The subject and data pertaining to binary mixtures, and higher orders, are presented in considerable detail, although in a somewhat disjointed manner throughout the book. Also, the subject of dephlegmation and rectification is developed in a simple way sufficient for the liquid mixtures following Raoult's law. A well-drawn set of about three dozen (T, x) and (p, x) curves is given for important binary and ternary mixtures. The author does not fail to emphasize the great need for systematic measurements and general scientific research in this field.

The final chapters deal briefly with the problems of coke-oven gas separation, the industrial importance of methane, and the problem of helium recovery. The final chapter is a brief sketch of the progress made in separating olefins in pure state from cracker gas.

The volume is the first of its kind in English and it should assist greatly in promoting interest in the industrial significance and value of applications of low temperature refrigeration.

F. G. KEYES

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POLAROGRAPHY. *I. M. Kolthoff*, Professor and Head of Division of Analytical Chemistry, University of Minnesota, and *J. J. Lingane*, Instructor in Chemistry, University of California. First Edition. Interscience Publishers, Inc., New York City, 1941. xvi + 510 pp. 141 figs. 15 × 23 cm. $6.00.

This first English book on the polarographic method of analysis will be welcomed by many who have been obliged to consult monographs in foreign languages or the more than 700 journal articles dealing with this subject. The authors have examined critically the majority of these and combined them into an excellent account of the present status of this new method. The book is dedicated to Professor Jaroslav Heyrovský, the "Originator of Polarographic Analysis," and is divided into eight parts. These are: I. Introduction (12 pp.); II. Theoretical Principles (200 pp.); III. Apparatus and General Technique (42 pp.); IV. and V. Inorganic and Organic Polarographic Analysis (86 and 62 pp.); VI. Biological Applications of Polarography (24 pp.); VII. Voltammetry with Platinum Microelectrodes (18 pp.); and VIII. Amperometric Titrations (34 pp.). An appendix (11 pp.) contains a list of reference electrode potentials and a table and chart of half-wave potentials of inorganic substances. This appendix may be bought separately for $0.75, but is best used in conjunction with the main text since it includes no literature references.

The theoretical part of the book is undoubtedly the most outstanding. It not only contains an all-inclusive discussion of the various factors which may influence the polarographic current–voltage curves, but also treats related topics, such as diffusion in general and the electrocapillary curve of mercury. This exposition of polarographic theory is beautiful and logical throughout, although it does not take into account the historical development of the science. This material will be much appreciated by a student of theoretical chemistry. However, one who wishes to make an occasional application of the polarographic method will have difficulty in picking out the essentials from the wealth of detail.

The remainder of the book is devoted to the practical aspects of polarography. Only a sketchy description of available apparatus is given. This is followed by a compilation of the many inorganic and organic analyses which have been studied. Since most of these are not yet practical and have only been tested in pure solutions, numerous references are given to aid the investigator in the development of suitable technics. The need for these is apparent, since less than two dozen tested practical procedures are described and it is pointed out that even these might be improved and simplified.

The last two parts of the book deal with more recent technics which were developed on the basis of experience gained in polarographic studies with the dropping mercury electrode. They show good promise but as yet have only limited applicability. In these chapters, the authors confine themselves mainly to their own extensive work in which voltammetry stands for polarography and amperometric stands for the more widely used term polarometric.

The book is well written and amply illustrated; it will be indispensable to anyone specializing in polarography.

OTTO H. MÜLLER

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NEW YORK CITY

ANNUAL REVIEW OF BIOCHEMISTRY. Volume X. *James Murray Luck*, Editor, Stanford University; *James H. C. Smith*, Associate Editor, Carnegie Institution of Washington, Division of Plant Biology, Stanford University. Annual Reviews, Inc., Stanford University, California, 1941. xi + 692 pp. 15 × 23 cm. $5.00.

This volume is the usual competent, authoritative review of biochemistry, though the work this year has been hampered somewhat by the discontinuance and delay in transit of foreign journals. The topics treated are: Biological Oxidations and Reductions; Proteolytic Enzymes; Nonproteolytic Enzymes; Chemistry of the Carbohydrates and Glycosides; Chemistry of Amino Acids and Proteins; The Chemistry and Metabolism of the Compounds of Sulfur; Carbohydrate Metabolism; Fat Metabolism; The Metabolism of Proteins and Amino Acids; The Biochemistry of the Nucleic Acids, Purines, and Pyrimidines; The Biochemistry of Creatine and Creatinine; Detoxication Mechanisms; Hormones; The Water-Soluble Vitamins; Fat-Soluble Vitamins; Nutrition; Relation of Soil and Plant Deficiencies and of Toxic Constituents in Soils to Animal Nutrition; Mineral Nutrition of Plants; Plant Growth Substances; Spectrometric Studies in Relation to Biology; Review of Bioluminescence; The Chemistry and Metabolism of Bacteria; Biochemical Nitrogen Fixation; Properties of Protein Monolayers.

The volume is also provided with author and subject indexes.

PRINCIPLES OF INORGANIC AND ANALYTICAL CHEMISTRY. *Ernest J. Baldwin*, Professor of Chemistry, University of Idaho (Southern Branch). Part I, Properties of Atoms and Molecules; Part II, Theory of Reactions. D. Van Nostrand Co., Inc., New York City, 1940. viii + 506 pp. 113 figs. 14.5 × 22.5 cm. $3.25.

This textbook, which primarily is intended for second-year students, is more than a book on analytical chemistry. As a matter of fact the book might be classified as a textbook of elementary physical chemistry rather than one written about inorganic chemistry. The text is divided into two parts, either of which may be considered first during the teaching of a course. The first part, about 200 pages, is essentially a discussion of the kinetic theory, atomic and molecular weights, solutions, atomic structure, and the periodic classification, the electron theory of valency, and nuclear chemistry. The author has done an excellent job of presenting some of the more recent developments of chemistry, but it is unfortunate that he did not go further toward a more complete treatment of certain of the topics. This is particularly true in the discussion of radioactive changes and nuclear chemistry.

Part II deals with reaction velocities, equilibrium, ionization, precipitation, hydrolysis, oxidation-reduction—in other words, the topics of analytical chemistry. Many illustrative problems, given in detail, add strength to the discussion. The hydronium ion is utilized in the discussions of hydrolysis, indicators, and related topics, although the simple hydrogen ion is frequently used in the discussion of oxidation-reduction reactions. The chapters on oxidation-reduction exhibit weaknesses which are probably due to an attempt to shorten the discussion. This is most evident in the sections on galvanic cells. The method of balancing oxidation-reduction reactions outlined is the one utilizing valence change. After having developed the material on electrode potentials in connection with oxidation-reduction, it seems regrettable that a method involving ion-electron reactions was not also included, since experiment shows that such changes actually occur.

The style in which the book is written is pleasing. The importance of developing a broad point of view is emphasized throughout the text.

Illustrative problems, given in detail, are very helpful. A more extensive discussion in a few places would clarify some of the points which are confusing. The book is essentially a discussion of principles to assist the student in gaining further knowledge of the science of chemistry.

LAURENCE L. QUILL

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THE ANALYTICAL CHEMISTRY OF INDUSTRIAL POISONS, HAZARDS AND SOLVENTS. *Morris B. Jacobs*, Ph.D., Department of Health, City of New York. First Edition. Interscience Publishers, Inc., New York City, 1941. xviii + 661 pp. 110 figs. 15 × 23 cm. $7.00.

This work is Volume I of "Chemical Analysis," a new series of monographs on analytical chemistry and its applications being prepared under the supervision of an editorial board consisting of the eminent analysts B. L. Clarke, I. M. Kolthoff, and H. H. Willard.

The author's professed objective was to present the most significant chemical aspects of the subject of industrial hygiene, with particular reference to the analytical chemistry of industrial poisons, hazards, and solvents. The material, much of which has appeared since the first World War, previously was largely scattered through periodicals and governmental bulletins.

Following an introduction and certain general instructions on sampling and on handling gases, the remaining 15 of the total 19 chapters are devoted to some 150 substances constituting possible health problems in the field of industrial hygiene. Representative classes of materials are dusts, metals, inorganic gases, and aliphatic and aromatic hydrocarbons and their derivatives. The chapter on halogenated hydrocarbons, for example, covers 24 compounds. Separate treatment is accorded chemical warfare agents. Much useful information is summarized in the 15 tables in the appendix.

For each of the substances there is a brief statement concerning its occurrence, properties, and importance for the health of one exposed to it. These facts are followed by the details of the analytical procedures considered best for determining the amount of the substance likely to be encountered. In general, the methods seem to have been well chosen, and they are adequately presented for the use of trained analysts.

Although the book is primarily a valuable compilation of analytical methods used in industrial hygiene, the general material, together with the bibliographies at the ends of the chapters, should be of interest to many teachers of chemistry.

M. G. MELLON

PURDUE UNIVERSITY
LAFAYETTE, INDIANA

LABORATORY MANUAL OF PHYSICAL CHEMISTRY. *Albert W. Davison*, Professor of Chemical Engineering, *Henry S. van Klooster*, Professor of Physical Chemistry, and *Walter H. Bauer*, Assistant Professor of Physical Chemistry, Rensselaer Polytechnic Institute. Third Edition. John Wiley and Sons, Inc., New York City, 1941. viii + 236 pages. 46 figs. 21 × 27.5 cm. $2.50.

The third edition of this well-known manual embodies certain innovations making for maximum utility. These are the use of a spiral binder, an abundance of graph paper after the appropriate experiments and the appendix, and an unusual number of tables of data—twenty-four—in the appendix.

The experiments themselves, forty-seven in number, are carefully selected and well tested. Numerous figures and clear descriptions leave one in little doubt concerning procedure. The theoretical discussions are good. The most unusual experiments are those on the polarographic method and Longsworth's moving boundary apparatus.

It is regrettable that there are so few literature references and that full specifications are not given for the apparatus used in measuring dielectric constants. However, this book will undoubtedly accomplish the authors' purpose whenever used. It can be recommended for consideration by every teacher of physical chemistry.

MALCOLM M. HARING

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THE SPECIAL THEORY OF RELATIVITY. *Herbert Dingle*, D.Sc., D.I.C., A.R.C.S., Professor of Natural Philosophy, Imperial College of Science and Technology. Chemical Publishing Co., Inc., Brooklyn, N. Y., 1941. vii + 94 pp. 2 figs. 10 × 16.5 cm. $1.50.

Working from the fundamental principle of relativity: "There is no meaning in absolute motion," to the *special* or *restricted* theory of relativity, "There is no meaning in absolute velocity," the author goes into an expanded discussion of the latter. He considers a few of the more important experiments which, according to traditional physical ideas, might have been expected to lead to a knowledge of the absolute velocity of the Earth—*i. e.*, the velocity of the Earth through the ether. Their failure to do so is then examined to see what error in traditional ideas led to the belief that they would succeed, and hence to find the correction which must be made. It is found that this correction can be most simply expressed as a substitution, for what we have been accustomed to call the "length" of a body, of a slightly more complicated expression. This substitution must be made whenever length occurs, explicitly or implicitly, in a physical relation, and since every physical measurement that is made depends in part on measurement of length, all physical measurements are thereby affected. The main part of the work is then to determine, from consideration of the classical definitions of the various physical quantities—time, mass, velocity, force, etc.—all the necessary corrections to be applied to them.

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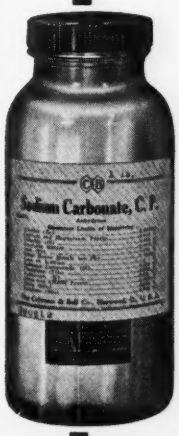

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